

SPECIFICATION

Electronic Version 1.2.8

Stylesheet Version 1.0

Limited-Play Optical Media With Improved Shelf-Life and Playability

Background of Invention

[0001] This application relates to limited-play optical media with improved shelf-life and playability.

[0002] There is a growing trend to utilize optical media for the storage and retrieval of data. This invention relates to machine-readable optical discs of all types, including compact discs, digital videodiscs – or digital versatile discs – (DVD's) and the like. Conventional optical discs have become widely used for storing digital information including music, video and movies.

[0003] In some applications, it is desirable to have a limited life for an optical disc. For example, music and movies on an optical disc are currently rented for a limited time period. When that time has expired, the disc must be returned. A need exists for machine-readable optical discs that do not need to be returned at the end of a rental period. Limited-play discs provide a solution to this problem. Limited play optical discs have been disclosed in U.S. 6,011,772, "Machine-Readable Optical Disc with Reading-Inhibit Agent", issued to SpectraDisc Corporation and in U.S. 5,815,484, "Copy Protectable, Optical Media Device and Methodology Therefore", issued to Hide and Seek Technologies, L.L.C. More recently, SpectraDisc Corp. has disclosed "Machine-Readable Optical Disc with Reading-Inhibit Agent" in US 6,343,063 and "Methods and Apparatus for Rendering an Optically Encoded Medium Unreadable" in US 6,338,933. U.S. 5,815,484 teaches that limited-play optical discs can be made by superimposing a film containing an oxygen sensitive, reduced form of a dye, including methylene blue, over the surface of the data structures on a disc. Upon exposure to

oxygen, the reduced form of the dye, which is essentially colorless, is oxidized to form the deep blue dye, methylene blue which interferes with the ability to read the optical medium.

[0004] Fig. 1 shows the layered structure of a non-limited play DVD of the type known in the art. The DVD has first and second outer polycarbonate layers (1, 2), sometimes referred to in the art as L_0 and L_1 , an adhesive layer (3) and an aluminum layer 4. Laser light is introduced through polycarbonate layer L_0 , (1) and reflects back from the aluminum layer (3) when the disc is played.

Summary of Invention

[0005] The present invention provides a limited-play optical medium with improved shelf stability. The optical medium is formed from a plurality of layers, including in sequence: (a) a first substrate layer; (b) a data layer; (c) a reflective layer; (d) a reactive layer comprising a dye having a reduced state and an oxidized state and further comprising an oxidized form of a reducing agent, said reducing agent being effective to convert the dye from the oxidized state to the reduced state, and (e) a second substrate layer.

[0006] The dye in the reduced state is substantially transparent to light of wavelengths used to read the optical medium, and the dye in the oxidized state absorbs light of wavelengths used to read the optical medium. The reflective metal layer is formed from a metal or metal alloy that is not significantly oxidized by the oxidized form of the reducing agent. For example, the reflective metal layer is suitably formed from silver or gold.

Brief Description of Drawings

[0007] Fig. 1 shows a cross-sectional view of a representative non-limited-play DVD in accordance with the prior art.

[0008] Fig. 2 shows a cross sectional view of a limited-play optical medium in accordance with the invention.

[0009] Fig. 3 shows a cross sectional view of a limited-play optical medium in accordance with the invention.

Detailed Description

[0010] The present invention provides a limited-play optical medium. Like non-limited play optical medium, the optical medium of the invention is formed from a plurality of layers, including in sequence: (a) a first substrate layer; (b) a data layer; (c) a reflective layer; (d) a reactive layer comprising a dye having a reduced state and an oxidized state and further comprising an oxidized form of a reducing agent, said reducing agent being effective to convert the dye from the oxidized state to the reduced state, and (e) a second substrate layer.

[0011] The dye in the reduced state is substantially transparent to light of wavelengths used to read the optical medium, and the dye in the oxidized state absorbs light of wavelengths used to read the optical medium.

[0012] In one embodiment of the limited-play optical medium of the invention, the dye used in the bonding layer is leuco methylene blue. To form leuco methylene blue, methylene blue is reduced during preparation of the reactive layer material by addition of a reducing agent. Since it is convenient to perform this reduction in a mixture including a bonding adhesive used in the reactive layer, any excess reducing agent and the oxidized form of the reducing agent both remain in the bonding layer upon assembly of the optical medium. Applicants have discovered that the oxidized form of the reducing agent (and potentially also the reduced form) can interact with and oxidize the metal reflective layer resulting in poor shelf life that has nothing to do with exposure of the dye in the limited-play optical medium to oxygen.

[0013] For example, a useful reducing agent which can be used to convert methylene blue to leuco methylene blue is tin (II) 2-ethylhexanoate. When these tin (II) compounds reduce methylene blue, they are oxidized to form tin (IV) species. These in turn are able to oxidize the aluminum alloys used in traditional optical medium, resulting in increased data error rates over time, specifically increased PISum8 errors. This limits the shelf life of such discs.

[0014] Through the identification of this problem and its source, the inventors have been able to provide improvements in the shelf life of limited-play optical medium. Specifically, in the optical medium of the invention, the reflective metal layer is formed from a metal or metal alloy which is not significantly oxidized by the oxidized form of

the reducing agent.

[0015] Fig. 2 shows the structure of one embodiment of the invention, which is a single sided, limited play optical medium. In this embodiment, there are two substrate layers (21, 22), reactive layer (23) which contains both a bonding adhesive and a dye, a reflective metal layer (24) and a data layer (25). Fig. 3 shows the structure of another embodiment of the invention. This structure is similar to that of Fig. 2 except that the reactive layer is present as an adhesive layer (32) and a acrylic coating/dye layer (33).

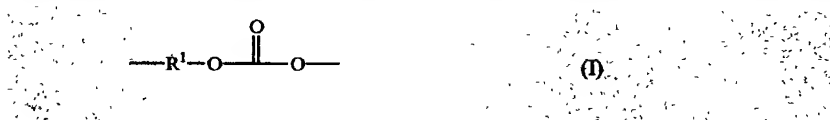
[0016] The substrate layers include at least one substrate on the read side of the optical medium (i.e., substrate 21) having low birefringence and high light transmittance at the read laser wavelength, i.e., is readable in an optical media device. Typically, the read laser wavelength is in a range between about 390 nanometers and about 430 nanometers (blue and blue-violet lasers) or in a range between about 630 nanometers and about 650 nanometers (red lasers). This substrate (21) comprises material having sufficient optical clarity, e.g., a birefringence of about ± 100 nm or less, to render the data storage material readable in a media device. In theory, any plastic that exhibits these properties can be employed as the read-side substrate (21). The other substrate (22) may be formed from the same material and have the same optical properties, but this is not required.

[0017] The plastic employed for both the first substrate and second substrate should be capable of withstanding subsequent processing parameters (e.g., application of subsequent layers) such as sputtering temperatures of about room temperature (about 25 ° C) up to about 150 ° C, and subsequent storage conditions (e.g., in a hot car having temperatures up to about 70 ° C). That is, it is desirable for the plastic to have sufficient thermal and mechanical stability to prevent deformation during the various layer deposition steps as well as during storage by the end-user. Possible plastics include thermoplastics with glass transition temperatures of about 100 ° C or greater, with about 125 ° C or greater preferred, about 140 ° C or greater more preferred, and about 200 ° C or greater even more preferred (e.g., polyetherimides, polyetheretherketones, polysulfones, polyethersulfones, polyetherethersulfones, polyphenylene ethers, polyimides, polycarbonates, etc.); with materials having glass transition temperatures greater than about 250 ° C more preferred, such as

polyetherimide in which sulfonedianiline or oxydianiline has been substituted for m-phenylenediamine, among others, as well as polyimides, combinations comprising at least one of the foregoing plastics, and others. Generally, polycarbonates are employed.

[0018] Some possible examples of first substrate and second substrate materials include, but are not limited to, amorphous, crystalline, and semi-crystalline thermoplastic materials such as: polyvinyl chloride, polyolefins (including, but not limited to, linear and cyclic polyolefins and including polyethylene, chlorinated polyethylene, polypropylene, and the like), polyesters (including, but not limited to, polyethylene terephthalate, polybutylene terephthalate, polycyclohexylmethyleneterephthalate, and the like), polyamides, polysulfones (including, but not limited to, hydrogenated polysulfones, and the like), polyimides, polyether imides, polyether sulfones, polyphenylene sulfides, polyether ketones, polyether ether ketones, ABS resins, polystyrenes (including, but not limited to, hydrogenated polystyrenes, syndiotactic and atactic polystyrenes, polycyclohexyl ethylene, styrene-co-acrylonitrile, styrene-co-maleic anhydride, and the like), polybutadiene, polyacrylates (including, but not limited to, polymethylmethacrylate (PMMA), methyl methacrylate-polyimide copolymers, and the like), polyacrylonitrile, polyacetals, polycarbonates, polyphenylene ethers (including, but not limited to, those derived from 2,6-dimethylphenol and copolymers with 2,3,6-trimethylphenol, and the like), ethylene-vinyl acetate copolymers, polyvinyl acetate, liquid crystal polymers, ethylene-tetrafluoroethylene copolymer, aromatic polyesters, polyvinyl fluoride, polyvinylidene fluoride, polyvinylidene chloride, and tetrafluoroethylenes (e.g., Teflons).

[0019] As used herein, the terms "polycarbonate" and "polycarbonate composition" includes compositions having structural units of the formula (I):

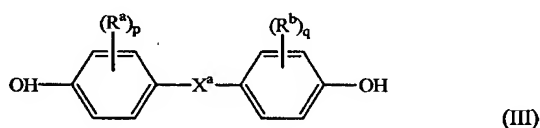


[0020] in which at least about 60 percent of the total number of R¹ groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Preferably, R¹ is an aromatic organic radical and, more preferably, a radical of the formula (II):

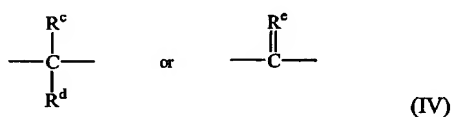


[0021] wherein each of A^1 and A^2 is a monocyclic divalent aryl radical and Y^1 is a bridging radical having zero, one, or two atoms which separate A^1 from A^2 . In an exemplary embodiment, one atom separates A^1 from A^2 . Illustrative, non-limiting examples of radicals of this type are ---O--- , ---S--- , ---S(O)--- , $\text{---S(O)}_2\text{---}$, ---C(O)--- , methylene, cyclohexyl-methylene, 2-[2,2,1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene, and the like. In another embodiment, zero atoms separate A^1 from A^2 , with an illustrative example being biphenol. The bridging radical Y^1 can be a hydrocarbon group or a saturated hydrocarbon group, for example, methylene, cyclohexylidene or isopropylidene or a heteroatom such as O--- or S--- .

[0022] Polycarbonates can be produced by the reaction of dihydroxy compounds in which only one atom separates A^1 and A^2 . As used herein, the term "dihydroxy compound" includes, for example, bisphenol compounds having the general formula (III) as follows:



[0023] wherein R^a and R^b each independently represent hydrogen, a halogen atom, or a monovalent hydrocarbon group; p and q are each independently integers from 0 to 4; and X^a represents one of the groups of formula (IV):



[0024] wherein R^c and R^d each independently represent a hydrogen atom or a monovalent linear or cyclic hydrocarbon group, and R^e is a divalent hydrocarbon group.

[0025] Some illustrative, non-limiting examples of suitable dihydroxy compounds include dihydric phenols and the dihydroxy-substituted aromatic hydrocarbons such as those disclosed by name or formula (generic or specific) in U.S. Patent No. 4,217,438. A nonexclusive list of specific examples of the types of bisphenol compounds that may be represented by formula (III) includes the following: 1,1-bis(4-hydroxyphenyl) methane; 1,1-bis(4-hydroxyphenyl) ethane; 2,2-bis(4-hydroxyphenyl) propane (hereinafter "bisphenol A" or "BPA"); 2,2-bis(4-hydroxyphenyl) butane; 2,2-bis(4-hydroxyphenyl) octane; 1,1-bis(4-hydroxyphenyl) propane; 1,1-bis(4-hydroxyphenyl) n-butane; bis(4-hydroxyphenyl) phenylmethane; 2,2-bis(4-hydroxy-3-methylphenyl) propane (hereinafter "DMBPA"); 1,1-bis(4-hydroxy-t-butylphenyl) propane; bis(hydroxyaryl) alkanes such as 2,2-bis(4-hydroxy-3-bromophenyl) propane; 1,1-bis(4-hydroxyphenyl) cyclopentane; 9,9-bis(4-hydroxyphenyl) fluorene; 9,9-bis(4-hydroxy-3-methylphenyl) fluorene; 4,4'-biphenol; and bis(hydroxyaryl) cycloalkanes such as 1,1-bis(4-hydroxyphenyl) cyclohexane and 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane (hereinafter "DMBPC" or "BCC"); and the like as well as combinations comprising at least one of the foregoing bisphenol compound.

[0026] It is also possible to employ polycarbonates resulting from the polymerization of two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with a hydroxy- or acid-terminated polyester or with a dibasic acid or with a hydroxy acid or with an aliphatic diacid in the event a carbonate copolymer rather than a homopolymer is desired for use. Generally, useful aliphatic diacids have carbon atoms in a range between about 2 and about 40. A preferred aliphatic diacid is dodecandioic acid.

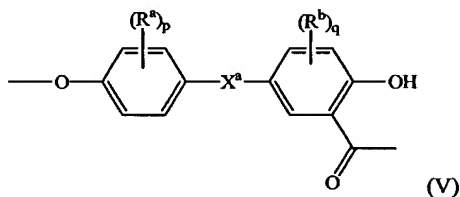
[0027] Polyarylates and polyester-carbonate resins or their blends can also be employed. Branched polycarbonates are also useful, as well as blends of linear polycarbonates and branched polycarbonates. The branched polycarbonates may be prepared by adding a branching agent during polymerization.

[0028] These branching agents are well known and may comprise polyfunctional organic compounds containing at least three functional groups which may be hydroxyl, carboxyl, carboxylic anhydride, haloformyl, and mixtures comprising at least one of the foregoing branching agents. Specific examples include trimellitic acid, trimellitic

anhydride, trimellitic trichloride, tris-p-hydroxy phenyl ethane, isatin-bis-phenol, tris-phenol TC (1,3,5-tris((p-hydroxyphenyl)isopropyl)benzene), tris-phenol PA (4(4(1,1-bis(p-hydroxyphenyl)-ethyl) α , α -dimethyl benzyl)phenol), 4-chloroformyl phthalic anhydride, trimesic acid, benzophenone tetracarboxylic acid, and the like, as well as combinations comprising at least one of the foregoing branching agents. The branching agents may be added at a level in a range between about 0.05 weight percent and about 2.0 weight percent, based upon the total weight of the substrate. Examples of branching agents and procedures for making branched polycarbonates are described in U.S. Patent. Nos. 3,635,895 and 4,001,184. All types of polycarbonate end groups are herein contemplated.

[0029] Preferred polycarbonates are based on bisphenol A, in which each of A¹ and A² is p-phenylene and Y¹ is isopropylidene. Preferably, the weight average molecular weight of the polycarbonate is in a range between about 5,000 atomic mass units and about 100,000 atomic mass units, more preferably in a range between about 10,000 atomic mass units and about 65,000 atomic mass units, and most preferably in a range between about 15,000 atomic mass units and about 35,000 atomic mass units.

[0030] In monitoring and evaluating polycarbonate synthesis, it is of particular interest to determine the concentration of Fries product present in the polycarbonate. The generation of significant Fries product can lead to polymer branching, resulting in uncontrollable melt behavior. As used herein, the terms "Fries" and "Fries product" denote a repeating unit in polycarbonate having the formula (V):



[0031] wherein R^a, R^b, p, and q are described in connection with Formula (III) and X^a is a bivalent radical as described in connection with Formula (III) given above.

[0032] The polycarbonate composition may also include various additives ordinarily incorporated in resin compositions of this type. Such additives are, for example, fillers

[0033] The reactive layer can be formed as a single layer (i.e., as a mixture of an adhesive system and a dye), or it can be formed from more than one layer (i.e., a dye-containing coating and a separate adhesive bonding layer). When a dye-containing bonding adhesive layer is used in the optical medium of the invention, it may be formed using a standard adhesive or an active adhesive (for example the TIPSOC system) in which a specially formulated adhesive is used in the bonding process.

[0035] Some epoxy resins, which can be used as the carrier, include monomeric, dimeric, oligomeric, or polymeric epoxy material containing one or a plurality of epoxy functional groups. Examples include reaction products of bisphenol-A and epichlorohydrin, epichlorohydrin with phenol-formaldehyde resins, and the like. Other organic resins can be in the form of mixtures of polyolefin and polythiols, such as shown by Kehr et al, U.S. Patent Nos. 3,697,395 and 3,697,402.

[0036] The term thermoplastic acrylic polymers, as used herein, is meant to embrace within its scope those thermoplastic polymers resulting from the polymerization of one or more acrylic acid ester monomers as well as methacrylic acid ester monomers. These monomers are represented by the general Formula VII:



[0037] wherein W is hydrogen or a methyl radical and R^f is an alkyl radical, preferably an alkyl radical comprising carbon atoms in a range between about 1 and about 20.

non-limiting examples of alkyl groups represented by R^f include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, hexyl, and the like.

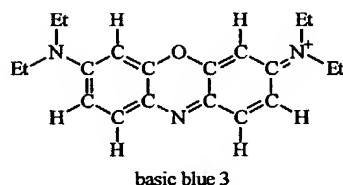
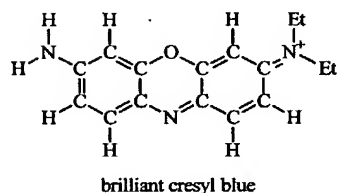
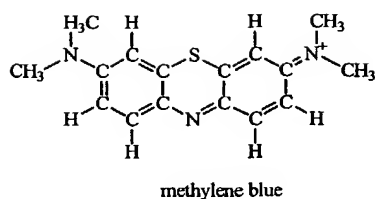
[0038] Some non-limiting examples of acrylic acid ester monomers represented by Formula VII include: methyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, and the like. Some non-limiting examples of methacrylic acid ester monomers represented by Formula VII include: methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, isobutyl methacrylate, propyl methacrylate, and the like, as well as reaction products and combinations comprising at least one of the foregoing.

[0039] The reactive layer, typically comprises both a polymer matrix and a dye. The reactive layer should initially have sufficient transmission to enable data retrieval by the data storage media device and subsequently form a layer which inhibits data retrieval by that device (e.g., which absorbs a sufficient amount of incident light, reflected light, or combinations thereof at the wavelength of the laser in the given device). Typically a layer that allows an initial percent reflectivity from the reflective layer of about 50% or greater can be employed, with an initial percent reflectivity of about 65% or greater preferred, and an initial percent reflectivity of about 75% or greater more preferred. Once the media has been exposed to oxygen, e.g., air, for a desired period of time (e.g., the desired allowable play time of the media), the layer preferably comprises a percent reflectivity of about 45% or less, with about 30% or less preferred, about 20% or less more preferred, and about less than 10% especially preferred.

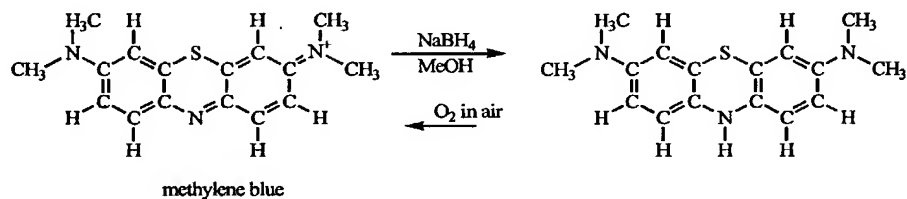
[0040] The adhesive layer component of the reactive layer can comprise any material which is capable of forming a layer penetrable by oxygen and which does not substantially interfere with the transfer of light through the media from and to the data retrieval device (e.g., that is substantially transparent at the wavelength of light utilized by the device, and/or which allows a reflectivity from the media of about 50% or greater, with a percent reflectivity of about 65% or greater preferred and a percent reflectivity of about 75% or greater more preferred). Additional adhesive layers of similar make-up can be included in the optical medium to further bind the other layers together. Suitable adhesive materials include UV materials such as acrylates (e.g., cross-linked acrylates, and the like), silicon hardcoats, and the like, as well as reaction products and combinations comprising at least one of the foregoing materials. Other examples of UV materials are described in U.S. Patent Nos. 4,179,548 and 4,491,508, which are incorporated herein by reference. Some useful monoacrylate monomers include butyl acrylate, hexyl acrylate, dodecyl acrylate and the like. Some useful polyfunctional acrylate monomers include, for example, diacrylates, triacrylates, tetraacrylates, and combinations thereof.

[0041]

Suitable dyes include oxygen sensitive leuco or reduced forms of methylene blue, brilliant cresyl blue, basic blue 3, and toluidine O, as well as reaction products and combinations comprising at least one of the foregoing materials; the structures of which are set forth below:



[0042] The method of synthesis and the oxygen dependent reoxidation to form the colored form of the methylene blue dye is shown below:



[0043] Typically, the critical reflectivity at which the limited play storage medium becomes playable (or unplayable) is less than about 20%, and more typically, the critical reflectivity is less than about 10%. In a preferred embodiment, the dye employed is triisopropylsilyloxycarbonyl-leucomethylene blue (TIPSOC). The preparation of this compound and its use in limited pay DVD's is described in a US Patent Application of FlexPlay Inc. which claims priority from US Provisional Application No. 60/295903, filed June 5, 2001, which is incorporated herein by reference. The text of this reproduced in Appendix A.

[0044] To reduce the dye and maintain the dye in the reduced state during assembly of the optical medium, and in some cases to control the rate of oxidation of the reduced dye on later exposure to air, the adhesive layer contains a reducing agent, and also the oxidized form of this reducing agent. For example, the adhesive layer may contain tin (II) 2-ethylhexanoate as a reducing agent, and the oxidized tin (IV) oxidized form thereof. Other Tin(II) compounds with ligands that are more soluble in the dye-containing coating solution or adhesive may also be used, for example, reducing agents from the list Tin(II)oxide, Tin(II)acetate, Tin(II)methanesulfonate, Tin(II)oxalate, Tin(II)phthalocyanine Tin (II) chloride. Other suitable reducing agents include, without limitation, Copper (I) derivatives such as ethylcyclopentadienyl(triphenylphosphine) copper(I), [Bis(trimethylsilyl)acetylene] (hexafluoroacetylacetonato)copper(I), bis (triphenylphosphine)copper(I) borohydride, Copper(I) thiophenolate, Copper(I) trifluoromethanesulfonate toluene complex, Copper(I) trifluoromethanesulfonate benzene complex, Hydrido(triphenylphosphine)copper(I), hexamer. Electron rich conjugated polymers or oligomers with a low redox potentials may also be used, for example poly(3,4-alkylenedioxythiophene) and poly(3,4-alkylenedioxyppyrrrole) derivatives. Furthermore, other reducing agents may be employed including hydrazine, phenylhydrazine, sodium borohydride, ascorbic acid, dithiocresol, glutathione, dithiothreitol, or 1,2,3,4-tetrahydroquinoline and commonly used reducing agents such as those listed in Reagents for Organic Synthesis, by Fieser & Fieser, John Wiley, 1967.

[0045] The reflective metal layer is formed by sputter coating one of the polycarbonate layers with a reflective metal. The metal employed is selected to provide adequate reflectivity for use as a data bearing substrate. In addition, in the optical medium of the invention, the metal is selected such that it is not significantly oxidized by the oxidized form of the reducing agent contained in the adhesive layer. As used herein, the term "not significantly oxidized" refers to levels of oxidation which are sufficiently low that they do not result in greater than a 50% increase in PISum8 data error rates upon 24 hours again at 55 E C/50% RH. In general, this level of resistance to oxidation can be achieved by selecting the metal or metal alloy such that it has a redox potential that is sufficiently different from the redox potential of the oxidized form of the reducing agent employed. In preferred embodiments of the invention, this difference

is at least 0.35 V. In specific embodiments, for example those employing tin(II) 2-ethylhexanoate as a reducing agent, the redox potential for the reaction $M^{+n} + n e^{-} \rightarrow M^0$ will be at least 0.5 V. Suitable metals for substantially any reducing agent which might be employed include silver, gold, platinum, palladium and silicon and mixtures thereof. In addition, alloys comprised of the foregoing metals combined with minor amounts of other metals may be used as long as the redox potential is at least 0.5 V.

[0046] In the course of making the present invention, the inventors observed that the initial reflectivity of the metal layer could substantially influence the play time of the optical medium of the invention. Thus, in a further aspect of the invention, there are provided limited-play optical play media, wherein the reflective layer has an initial reflectivity of at least 70%, as can be achieved using gold- and silver-based reflective layers. In addition, the invention provides a method for increasing the play time of a limited play optical medium, comprising the step of preparing a limited-play optical medium comprising a reflective layer formed from a metal or metal alloy, wherein the initial percent reflectivity from the reflective layer of about 65% or greater, with an initial percent reflectivity of about 70% or greater preferred, and an initial percent reflectivity of about 75% or greater more preferred. In this context, "play time" is defined as the total time in which the limited-play data storage medium plays generally without error in the playback device.

[0047] The optical medium is assembled by adhering the sputter-coated surface of the one polycarbonate layer to the other polycarbonate layer with the dye-containing adhesive bonding layer. The adhesive bonding layer may be formed on the second polycarbonate layer or on the metal layer before assembly.

[0048] The invention will now be further described with reference to the following non-limited examples.

[0049] *Example 1* Preparation of PMMA/Leuco Methylene Blue Coating Solution To a 1000 mL, single-necked round bottom flask equipped with a heating mantle and magnetic stirrer was added 375 grams of Dowanol PM (1-methoxy-2-propanol). Elvacite 2010 beads, 75 grams, were then added slowly with rapid stirring to avoid making clumps. The mixture was heated to reflux under nitrogen and stirred under reflux for 10

minutes to decompose any remaining azo initiator residues. After cooling, the polymer solution was filtered through an 0.1 micron Whatman Polycap 75 TF capsule with several psi house-nitrogen pressure, and stored in a clean 500 mL Nalgene bottle.

[0050] In a 100 mL single-necked, round-bottomed flask was added 1.2 grams of methylene blue trihydrate, 800 mg camphorsulfonic acid, and 40 grams of Dowanol PM. The mixture was briefly heated to reflux with stirring under nitrogen, and the flask was then capped with a rubber septum while still hot. The septum was penetrated by a syringe needle connected to an argon bubbler. With continued stirring, 5.2 grams of stannous octanoate was added by syringe. Solids mostly dissolved and the dye bleached, thereby producing a dark amber solution. FC-431 (600 microliters, #M coating additive) was then added by syringe with stirring, and the rubber septum was secured to the flask with copper wire.

[0051] To a 1000 ml single-necked, round-bottomed flask was added 360 grams of the filtered PMMA/Dowanol PM solution. This solution was stirred under reflux and argon for approximately 10 minutes to eliminate dissolved oxygen, and was allowed to cool to room temperature under argon. The flask was then fitted with a rubber septum penetrated by a syringe needle connected to a nitrogen bubbler. A cannula filter was prepared by connecting two # 18 syringe needles, 10 inches, in length, to a Gelman Acrodisc CR syringe filter (25 mm diameter, 0.2 micron PTFE membrane) with a male-to-male Luer adapter on the high-pressure side. The high-pressure end was inserted into the septum of the 100 ml flask above the leuco methylene blue solution, the cannula was flushed with argon, and then the other end was inserted into the 1000 mL flask above the deoxygenated PMMA solution. The cannula was then inserted into the leuco methylene blue solution, and that solution was transferred into the stirred PMMA solution through the 0.2-micron filter by applying argon pressure. The resulting clear, dark-amber coating solution was poured into two clean, clear-glass bottles in a nitrogen-filled cabinet.

[0052] *Example 2* This example illustrates the preparation of PMMA/leuco methylene blue coating solution by a one-pot method.

[0053] A solution of PMMA in 1-methoxy-2-propanol was prepared by stirring under

nitrogen a mixture of 8.3 grams of Elvacite 2008 PMMA and 2.8 grams of Elvacite 2010 PMMA in 60 grams of 1-methoxy-2-propanol heated to ~70 ° C. To the solution was added 0.11 mL of BYK-301, 0.48 grams of methylene blue trihydrate, 0.20 grams of camphor sulfonic acid followed by 2.09 grams of TinII 2-ethylhexanoate. After cooling to ambient temperature, the solution was ready for use.

[0054] *Example 3* To prepare a coated disc, approximately 3.5 mL of the Example 1 PMMA/leuco methylene blue coating solution was applied as a ring around the inner diameter of a DVD held on a spin coater and spun at 500 rpm for 60 seconds; the coating was tack-free and essentially colorless. The coating thickness ranged from about 4 microns to 5 microns from the inner radius to the outer radius of the disc.

[0055] *Example 4* To prepare a coated disc, approximately 3.5 mL of the Example 2 PMMA/leuco methylene blue coating solution was applied as a ring around the inner diameter of a DVD held on a spin coater and spun at 500 rpm for 60 seconds; the coating was tack-free and essentially colorless.

[0056] *Example 5* This example illustrates the preparation of the dye solution by an alternate one-pot process. To a one liter round bottom flask equipped with an overhead stirrer, a nitrogen inlet tube, and a nitrogen outlet connected to a bubbler was added 655.7 grams of 1-methoxy-2-propanol. To the flask was added 10.86 grams of methylene blue trihydrate and 5.45 grams of camphor sulfonic acid. Nitrogen was bubbled through the solution for about 15 minutes while heating to ~80 ° C after which time 47 grams of Tin (II) 2-ethylhexanoate were added. The Tin (II) can be added either by pouring directly into the solution or by pumping into the solution as long as the solution is kept free of air. After stirring for 20 minutes at ~80 ° C, 127.1 grams of Elvacite 2008 PMMA were added in increments to the stirred solution followed by 1.2 mL of BYK-301 and 12.7 grams of biphenol. The solution was stirred while cooling. To filter the solution a fritted glass funnel (ASTM 40-60) made to hold larger volumes (1 liter) equipped with a gas inlet port was fitted to a vacuum filter flask. Vacuum was pulled through the flask and funnel while nitrogen was blown through the inlet port in order to de-aerate both vessels. The coating solution was then poured into the fritted glass funnel while being swept with nitrogen and filtered. To transfer the solution to a storage bottle, the bottle was first de-aerated by

sweeping with nitrogen (or argon) at 50 mL/sec for about a minute. The solution was transferred in air by pouring the solution under a stream of nitrogen into the de-aerated bottle. After transfer was complete, the solution was sparged at ~50 mL/sec for 15 seconds after which time the bottle was capped and taped shut. (Ideally this operation should be made by pumping or pressure transfer to keep the solution in an inert environment at all times.) *Example 6* Samples C1–C8 were prepared using a polymer/dye solutions containing leucomethylene blue, tin(II) 2-ethylhexanoate, polymethylmethacrylate and Dowanol PM as described in Example 1. The samples were spin-coated using a Headway laboratory spinner to the data layer of DVD half disks (0.6 mm polycarbonate substrates sputtered with the metal indicated in the table below to thicknesses sufficient to yield approximately 60–70% optical reflectivity). After the spin-coating operation, the coated substrates were bonded to a 0.6mm polycarbonate substrate using a UV-crosslinked acrylate (Daicure SD698). The samples were then allowed to deaerate in nitrogen for 24 hours prior to packaging. Samples were removed from the packaging and electrical measurements (PI Sum8 ECC) were made on the samples using a CD Associates DVD200MG Plus DVD analyzer. The samples were then repackaged under nitrogen and placed into a humidity oven at 55 °C/50% relative humidity for 24 hours. The samples were then removed from the packaging and remeasured using the DVD analyzer. Results from the PI Sum8 ECC measurements before and after the aging tests are tabulated below in Table 1. Samples C1–C3 showed substantial corrosion of the Al-sputtered reflective layer after aging. In comparison, the samples (C4–C8) with the Ag- and Au-sputtered reflective layers showed substantially less corrosion and stable PI Sum8 ECC errors. In addition, a sample (C9) was prepared using a non-coated Al-sputtered substrate. This reference sample also showed stable PI Sum8 ECC errors. Finally, a sample (C10) was prepared under more clean coating conditions using a modified CD-R spin-coater to apply the leucomethylene blue-containing coating and bonded using a Steag DVD-line. Even under these manufacturing conditions, there was a substantial increase in the PISum8 ECC error after aging.

[t1]

Table 1

Sample	Reflective Layer Metal	PI Sum8 ECC Error Before Aging	PI Sum8 ECC Error After Aging	
C1	Al	510	N.A.	Translucent Reflective Layer (severe corrosion)
C2	Al	477	N.A.	Translucent Reflective Layer (severe corrosion)
C3	Al	589	N.A.	Translucent Reflective Layer (severe corrosion)
C4	Ag	850	623	
C5	Ag	871	658	
C7	Au	996	724	
C8	Au	N.A.	914	
C9	Al (non-coated)	568	609	
C10	Al	67	1651	

[0057]

Example 7 Non-metallized and metallized (sputtered as specified in the table below) half disc (data bearing) were placed in inert (N₂) atmosphere 24 hr prior to coating. These metallized half discs were coated using a solution prepared from: a 598.4g aliquot of a PMMA Solution prepared from Dowanol PM (26383.9 g) and PMMA Elvicate (635. 6g); Methylene blue trihydrate (54.3 g) Camphorsulphonic acid (27.27g) Stannous Octanoate (235.33g) BYK-301 (6.02(g)) Biphenol (63.50g) added after the dissolution of the above mixture Discs were then bonded using Daicure SD698 adhesive as described in Example 6. The aluminum-sputtered samples were prepared using a laboratory Headway spin-coater while the silver- and gold-sputtered disks were prepared on a Steag DVD manufacturing line. Electrical properties were measured on a periodic bases as described in Table 2 with the samples being stored in a nitrogen box between measurements.

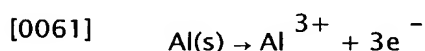
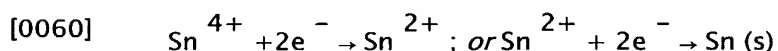
[t2]

Table 2

PI Sum 8 Max			
Sputtering			
Target	As Bonded	After 6 days	% Change
Al	54	1596	2856
Al	280	1550	454
Al	56	984	1657
Ag	799	626	-22
Ag	506	501	-1
Ag	607	627	3
Ag	524	481	-8
Ag	522	585	12
Au	628	744	18
Au	551	503	-9
Au	969	669	-31
Au	466	791	70

[0058] *Example 8* TIPSOC DVD samples were prepared and analyzed by AFM. The samples contained either 0% or 4% tin(II) 2-ethylhexanoate and were prepared for analysis by delamination to expose the Al surface. The topography of the sample having no tin(II) 2-ethylhexanoate imaged well, with metal grains clearly defined. The smooth edges of the pits could clearly be observed. The topography of the sample with 4% tin had 75 nm wide/25 nm high features which made the surface very difficult to image. The edges of the pits were less well defined as for the sample having no tin.

[0059] Part of the 4% tin(II) 2-ethylhexanoate, which was present in the adhesive, reduces methylene blue (which was formed during the manufacturing process) back to leuco methylene blue. During that reaction Sn^{4+} is formed. The observed deterioration (corrosion, rusting) of the disc subsequently can be due to the following redox reactions:



[0062] *Example 9* TIPSOC based DVD samples containing with active adhesive containing TIPSOC and 4% tin(II) 2-ethylhexanoate were prepared on a modified M2 bonder equipment. Aluminum alloy and Gold were used as sputtering targets for comparative purposes. The samples were kept in dry nitrogen atmosphere at room temperature

between measurements. Changes to the measured PI Sum 8 values are noted in Table 3 below:

[t6]

Table 3

Sputtering	PI Sum 8 Max		
Target	As Bonded	7 Days after	% Increase
Al	93	335	260
Al	89	267	199
Al	75	280	273
Al	72	287	296
Al	67	223	232
Al	62	261	318
Au	43	37	-14
Au	65	43	-34
Au	57	33	-42
Au	67	42	-37
Au	51	40	-20
Au	61	35	-42

[0063]

Example 10 DVDs with silver reflective layers have an extended play time relative to the DVDs with gold reflective layers due to the higher initial reflectivities of the silver reflective layers (~81%) versus the gold reflective layers (~70%), and both have superior properties as compared to aluminum.. Disks were prepared in a fashion similar to those made for Example # 9. The results are summarized in Table 4.

[t3]

Table 4

Sample	Deblocking Condition	L. I Metal	Refl at start of measurement (ave@41nm)	Time To R=45%	Time to R=20%	Time to R=10%
1	24hr/55oC/wet	Ag	81.64	8.44	19.84	25.11
2	24hr/55oC/wet	Au	69.75	6.54	17.75	23.27
3	24hr/55oC/wet	Au	69.71	6.70	18.11	23.37
4	72hr/55oC/wet	Ag	82.05	6.49	15.49	22.50
5	72hr/55oC/wet	Au	69.65	5.71	14.21	22.63
6	72hr/55oC/wet	Au	70.1	5.72	13.47	21.16
7	Room Temp	Ag	80.79	11.19	22.88	27.31
8	Room Temp	Au	69.16	8.49	21.16	26.02
9	Room Temp	Au	69.63	8.73	21.35	26.17

[0064] APPENDIX I

[0065] *LIMITED PLAY OPTICAL DEVICES WITH INTERSTITIAL REACTIVE LAYER AND METHODS OF MAKING SAME*

[0066] Priority is herewith claimed under 35 U.S.C. § 119(e) from copending Provisional Patent Application 60/295903, filed June 5, 2001. The disclosure of this Provisional Patent Application is incorporated by reference herein in its entirety.

[0067] *FIELD OF THE INVENTION*

[0068] This invention relates to optically readable data storage media and, more particularly, to methods, compositions, and articles of manufacture of optically readable data storage media wherein the data is accessible for a finite period of time.

[0069] *BACKGROUND OF THE INVENTION*

[0070] Optical discs such as CDs and DVDs are sold and rented to consumers. The content of the optical discs may be music, movies, video clips, software or data. The purchase price of CDs and DVDs can be high; this reflects the value of the information encoded on the discs, such as movies or software, rather than the manufacturing cost of these optical discs. Frequently, content providers, such as movie studios or software companies, do not want to sell at a low cost copies of their information that

will have a long lifetime in the marketplace. Consumers frequently want to access content information only for a brief period and at a low cost. Rentals of CDs and DVDs enable consumers to access content information at a lower cost than if consumers had to purchase the media, but the need to return the physical media is inconvenient. It would be desirable to have limited play/expiring optical media that the user could purchase at a low cost, would address the concerns of the content providers about lifetime of their content in the marketplace, and which would not have the disadvantage of having to be returned, as is the case with videotape movie rentals today. It would also be desirable to manufacture such optical media at low cost and with minimum changes to existing manufacturing processes for optical discs. Finally, in order for the content providers to be willing to provide their content through limited play/expiring optical media, the mechanism that limits playing of the media should not be easily defeatable, enabling access to the content beyond the intended period of use.

[0071] Heretofore, the requirements of low cost, limited content lifetime, avoidance of rental returns, resistance to attempts to defeat, and minimum changes to existing manufacturing processes referred to above have not been fully met. What is needed is a solution that simultaneously addresses all of these requirements. One embodiment of the present invention is directed to meeting these requirements, among others.

[0072] Several approaches have been proposed to make a limited play (expiring) optical disc based on a layer that changes from a non-interfering ("transparent") state where it does not interfere with the reliable reading of the information on the optical disc to an interfering ("opaque") state where the layer interferes with the reading of the data on the optical disc (e.g., see U.S. Patent No. 5,815,484 assigned to Smith et al. and U.S. Patent No. 6,011,772 assigned to Rollhaus et al.). The interference may be due to the layer becoming dark, reflective, highly birefringent, pitting, bubbling, shattering, corroding, bending, changing refractive properties or combinations of these, among other possibilities.

[0073] Optical discs with such a layer changing from a transparent to an opaque state in response to a stimulus such as exposure to oxygen in the atmosphere, or the light of the reading laser, can be used to manufacture limited-play optical discs (such as

DVDs) that become unusable in a predetermined way (such as within a certain period of exposure to environmental oxygen). Such discs can find a variety of commercial applications, such as the viewing of a video by consumers at a moment chosen by the consumer and without the need to return the expired optical disc.

[0074] The interfering layer that renders the disc unplayable by inhibiting the reading of the data can be applied via a variety of techniques to the surface of an optical disc. Such an approach, however, has a number of disadvantages. For example, it may be defeated by finding a way to reverse the transition of the layer to an opaque state, such as exposing the disc to a reducing chemical substance that reverses an oxidation reaction, or by entirely removing the layer through chemical means (such as solvents) or mechanical means (such as polishing or grinding). Also, adding an additional layer can complicate manufacturing of the optical discs, for example by requiring additional capital equipment and additional steps in the manufacturing process, and thus can increase the costs and/or decrease the yields for the manufacturing of optical discs.

[0075] A protective layer engineered to resist attempts to defeat the disc can be applied on top of the interfering layer, an approach that has been used by at least some of the present inventors. However, this introduces still another step in the manufacturing process, further adding to costs and possibly further reducing manufacturing yields. Furthermore, since the protective layer would still be at the surface of the disc, it could still be removed by chemical means (such as solvents) or mechanical means (such as polishing or grinding), or could be defeated by chemical substances that could diffuse through the protective layer and reach the reactive layer.

[0076] As explained above, when manufacturing expiring optical discs, it is desirable to employ a cost effective manufacturing process and to make discs that are not easily defeatable. In addition, it is desirable for the disc to make a rapid transition from the playable to the expired state. Among other benefits, this would reduce the variation of the playing period among optical media players and drives, despite the fact that there is substantial variability in the ability of the players and drives in the market to play discs with a given deterioration in their physical playability characteristics (such as the reflectivity to the light of the reading laser).

[0077] *SUMMARY OF THE INVENTION*

- [0078] Under a first aspect of the present invention limited play optical devices are provided with an interstitial reactive layer and methods of making same.
- [0079] Under a second aspect of the present invention a method is provided for authoring a master to produce a substrate of a multi-substrate, optically-readable storage medium wherein a topology having a plurality of pits and lands is used to create an inverted version of the topology in which said inverted version of the topology is used as the topology of the master.
- [0080] Under a third aspect of the present invention a method is provided for forming a multi-substrate, optically-readable storage medium, wherein the medium has information defined as a plurality of pits and lands on an upper substrate and said information is to be read by light being transmitted through a lower substrate wherein an adhesive layer bonds the upper substrate and lower substrate together.
- [0081] Under a fourth aspect of the present invention a data storage device is provided having a first substrate having defined thereon a plurality of pits and lands covered by a reflective material and a second substrate wherein a bonding layer containing a reactive agent, which inhibits transmission of light in response to a predetermined stimulus, resides between the first substrate and the second substrate.
- [0082] Under a fifth aspect of the present invention an adhesive is provided for bonding a first substrate and a second substrate, wherein said adhesive comprises a carrier material and a reactive material that renders the data encoded substrate unreadable.
- [0083] Under a sixth aspect of the present invention a mechanism is provided that causes the data stored on an optically-readable data storage medium to first become unreadable and second destroyed.
- [0084] Under a seventh aspect of the present invention an optically-readable data storage medium is provided having a first substrate and a second substrate, wherein at least one of said first substrate and said second substrate has information encoding features, and a bonding layer between first substrate and second substrate in which said bonding layer comprises a carrier material and a reactive material where said reactive material changes from a transparent state to an optically opaque state as a

result of a predefined stimulus.

[0085] Under a eighth aspect of the present invention a method making an adhesive is provided for bonding a first substrate and a second substrate wherein a blocked dye is combined with a carrier material in which said blocked dye is subsequently unblocked resulting in the reduced form of the unblocked dye.

[0086] *BRIEF DESCRIPTION OF THE DRAWINGS*

[0087] FIG. 1 is a schematic cross sectional view of select stages in the process of creating a physical stamper used in replicating DVD-5 substrates.

[0088] FIG. 2 is a schematic cross sectional view of a single layer DVD-5 disc.

[0089] FIG. 3 is a schematic cross sectional view illustrating the manufacturing and reading of a standard DVD-5.

[0090] FIG. 4 is a diagram representing single sided single layer, single sided double layer, double layer single sided, and double layer double sided DVD constructs.

[0091] FIG. 5 is a graphic depicting the index of refraction as a function of substrate thickness for single layer and double layer DVDs.

[0092] FIG. 6 is a schematic illustrating the read-out possibilities for single-layer and dual-layer DVDs.

[0093] FIG. 7 is a schematic cross sectional view illustrating a modified DVD-5 construct with the bonding layer in the optical path of the reading laser.

[0094] FIG. 8 is schematic cross sectional view illustrating the manufacturing and reading of an altered DVD-5 construct with the bonding layer in the optical path of the reading laser in which the mother stamper was used to mold the L1 substrate.

[0095] FIG. 9 is a schematic cross sectional view illustrating the stamper reference plane of a standard DVD-5 construct wherein the pits and lands are molded in the L0 substrate.

[0096] FIG. 10 is a schematic cross sectional view illustrating the stamper reference plane of a modified DVD-5 construct wherein the pits and lands are molded in the L1

substrate.

- [0097] FIG. 11 is a graphic depicting an atomic force microscope image of a DVD-5 stamper.
- [0098] FIG. 12 is a graphic depicting an atomic force microscope image of a DVD-5 mother stamper.
- [0099] FIG. 13 is a graphic depicting an atomic force microscope image of the L1 layer of a modified DVD-5 that was molded from a mother stamper.
- [0100] FIG. 14 is a schematic cross sectional view illustrating the manufacturing and reading of a modified DVD-5 in which the L1 layer was molded from a father stamper wherein the direction of the spiral track was reversed during mastering.
- [0101] FIG. 15 is a schematic cross sectional view illustrating the stamper reference plane of a modified DVD-5 construct wherein the pits are above the surfaces of the lands and the lands are at the reference plane of the L1 substrate.
- [0102] FIG. 16 is a schematic cross sectional view illustrating the stamper reference plane of a modified DVD-5 construct wherein the pits are above the reference plane of the L1 substrate and the lands are at the reference plane of the L1 substrate.
- [0103] FIG. 17 illustrates a potential synthetic pathway for the synthesis of triisopropylsilyloxycarbonylleucomethylene blue.
- [0104] FIG. 18 illustrates the cyan reflectance density of optically readable storage media coated with triisopropylsilyloxycarbonylleucomethylene blue as a function of time in the presence 1,4-diazabicyclo[2,2,2]octane.
- [0105] FIG. 19 is a graphic depicting the spectral absorption of methylene blue.
- [0106] FIG. 20 is a schematic cross sectional view illustrating a modified DVD-9 construct, wherein the L0 layer is partially metallized.
- [0107] FIG. 21A and 21B are graphics depicting Koch test results for a modified DVD-5 construct wherein the pits are molded as depressions in the L1 substrate using a father stamper in which the direction of the spiral track is reversed during mastering.

[0108] *DETAILED DESCRIPTION*

[0109] Certain optical discs, such as DVDs, consist of two plastic halves ("substrates"), which are metallized and bound together with an interstitial bonding layer. It would be desirable to use an interstitial layer between the two substrates to interfere with the reading laser in order to inhibit reading of the disc. This would result in a disc that is more difficult to defeat, as the two halves of the optical disc would protect the interfering layer. Using an interstitial layer as the interfering layer still allows triggering the process of disc expiration. For example, polycarbonate, which is typically used to manufacture DVD substrates, allows the propagation of oxygen that could reach the interstitial reactive layer and trigger a reaction that causes the expiration of the disc.

[0110] Furthermore, it would be desirable to use the bonding layer itself as the interfering layer, for example by changing the chemical composition of the bonding layer through the incorporation of a reactive substance. This could simplify the manufacturing of limited-play optical discs because no additional layers would be introduced, and attempting to defeat the limited-play mechanism by removing this layer could destroy the optical disc itself, as the bonding layer is critical to the integrity of the optical disc. However, in certain types of optical discs, such as a DVD-5, the bonding layer is not in the optical path. FIG. 2 illustrates a cross sectional view of the layers typical of a DVD-5 construct. Thus while the bonding layer could play part in an expiration process for a DVD-5 that does not rely on direct interference with the reading laser (e.g., by corroding the reflective metal layer that is in contact with the bonding layer), it would not be possible to make this type of disc expire by transitioning the bonding layer to a state that prevents the reading laser from reading the data on the disc. Since it is often desirable to make the disc unplayable by means of a process that interferes with the reading laser, it is desirable to have a disc similar to a DVD-5 where the interstitial bonding layer is in the optical path.

[0111] In limited use optical discs where the expiration process relies on interference with the reading laser, the data encoding structures (such as metallized pits on a polycarbonate substrate) typically are preserved in an expired disc, although the reading laser is prevented from reading the encoded information. As long as these

data structures are present, there is always the possibility of the disc being defeated by enabling the reading laser to access the information. It would thus be desirable to have additional mechanisms that prevent recovery of the data, such as permanently erasing the data by compromising the integrity of the data structures on the optical disc.

[0112] These, and other, goals and embodiments of the invention will be better appreciated and understood when considered in conjunction with the following description and the accompanying drawings. It should be understood, however, that the following description, while indicating preferred embodiments of the invention and numerous specific details thereof, is given by way of illustration and not of limitation. Many changes and modifications may be made within the scope of the invention without departing from the spirit thereof, and the invention includes all such modifications.

[0113] A clear conception of the advantages and features constituting the present invention, and of the components and operation of model systems provided with the invention, will become more readily apparent by referring to the exemplary, and therefore non-limiting, embodiments illustrated in the drawings accompanying and forming a part of this specification. It should be noted that the features illustrated in the drawings are not necessarily drawn to scale.

[0114] We now describe the different aspects of the current invention, and several corresponding embodiments and examples.

[0115] DVDs are the most common optical discs used for distribution of movies. DVDs are made from two bonded plastic substrates, typically referred to as L0 for the bottom substrate and L1 for the top substrate, where "top" and "bottom" refer to a DVD in a playing position where it is read from the bottom, as is the common convention. These substrates are molded from materials such as polycarbonate, acrylic, or polyolefine, which is injected in a molten form to a mold and pressed against a stamper. The process of creating the physical stampers used in replicating the DVD substrates is referred to as Mastering. The following procedure is used, is illustrated in Figure 1:1. Float glass blank 5 is polished and coated with a primer 10 to enhance adhesion with the photo resist layer 15.

- [0116] 2.Photo resist coating 15 is applied, baked, and then exposed to the laser for recording. The formatted data signal is used to modulate the cutting laser of a laser beam recorder (LBR) machine which creates pits 20 in the glass disc.
- [0117] 3.The exposed glass is then developed leaving pits 20 and lands 25 across the surface.
- [0118] 4.This "Glass Master"then has a thin (110 nm) metal layer sputter-applied to make the surface conductive for electroplating.
- [0119] 5.The glass master is then placed into an electroplating solution where nickel is formed to the desired thickness. (Typically 0.300 mm).
- [0120] 6.This "Metal Father"(or "father stamper 30") is then separated from the glass master 35 and cleaned. At this step, the metal father 30 could be used for the molding process, but if the part gets destroyed or damaged in replication, the entire process must be repeated.
- [0121] 7.Therefore, most manufacturers will grow "Metal Mothers"(or "mother stampers 40"), which are negatives of the father 30. Typically, four mother stampers 40 can be grown from one father 30 without quality degradation, and from each mother 40, up to 8 stampers ("sons 45") can be grown.
- [0122] 8.Stampers get sent to replication facilities and mothers 40 are stored for reorders or replacement parts.
- [0123] In the case of a DVD-5, which is a single layer disc illustrated in Figure 2, the L0 substrate 100 is covered with a thin reflective layer 105 of aluminum by a sputtering process. This creates a metallic coating between 60 and 100 angstroms thick (the L0 layer). The L0 substrate 100 is then bonded 110 to a blank L1 substrate 110, as illustrated in Figure 3. For a DVD-9, which is a two-layer disc, the L0 layer is formed as a very thin, semi-reflective metal layer, and is typically made of gold. A fully reflective aluminum layer is formed on the L1 substrate (the L1 layer). The two substrates are subsequently bonded with appropriate adhesive material, which forms a transparent bonding layer, to form the DVD-9 disc.
- [0124] As seen in the DVD family illustration in Figure 4, a DVD disc may contain either

one or two information layers for each substrate, resulting to different types of disc capacities, such as DVD-5 200 (single sided, single layer, 4.7 Gbyte capacity), DVD-9 205 (single sided, dual layer, 8.5 Gbyte capacity), DVD-10 210 (double sided, single layer, 9.4 Gbyte capacity), DVD-14 (double sided, one side single layer, one side dual layer, 13.2 Gbyte capacity), and DVD-18 215 (double sided, dual layer, 17 Gbyte capacity).

[0125] A dual layer disc such as a DVD-9 205 must conform to the "DVD Specifications for Read-Only Disc, Part 1 Physical Specifications Version 1.0", which require the following:

1. Total Disc thickness, including bonding layer 110, spacer(s) and label(s), shall be $1.20\text{mm} + 0.30\text{ mm} / - 0.06\text{ mm}$
2. Index of refraction (RI) of the transparent substrate shall be 1.55 ± 0.10
3. The index of refraction of the spacer shall be (RI of the substrate ± 0.10)
4. Thickness of the transparent substrate is specified as a function of its index of refraction. Typically with polycarbonate at $RI = 1.56$, the thickness values for the disc substrate would be $0.57\text{ mm} \sim 0.63\text{ mm}$ (see Figure 5A and 5B)

There is no specification for the DVD-5 200 and DVD-10 210 spacer layer (bonding layer 110), as long as the total disc thickness conforms to the DVD specification and the half discs (molded substrates) conform to RI related specifications as above.

[0126] The information in DVDs is encoded in the pits 20 and lands 25 (data areas that are not pits) that are molded into the substrates and subsequently are metallized to form the corresponding data layer. The pits and the lands are organized in a spiral track, which, in the case of a DVD-5 200, is read in a clockwise direction beginning at the inside of the disc and proceeding towards the outside of the disc. The reference area of the disc that is not occupied by data is used for tracking of the reading laser. The reading laser, which has a wavelength of 630-650 nanometers in vacuum, is focused on the L0 layer 100 of a DVD-5 200 or DVD-9 205, or on the L1 layer 115 of a DVD-9 by penetrating through the semi-reflective L0 layer 100, and it is reflected back to a photo detector. During transitions from a pit 20 to a land 25 or vice versa, interference patterns develop, which are detected by the photo detector and result in changes in its electrical output. These changes in the electrical output of the photo detector allow the player to read the information recorded on the DVD.

[0127] Dual-layer discs, such as DVD-9s 205, typically utilize one of two methods for read-out of the disc information: A dual-layer Parallel Track Path (PTP) disc 299 will have a Lead-in 300 and a Lead-out 305 area on both layers, as illustrated in Figure 6. For each layer, the lead-in 300 area is located at the inner radius of the disc, and lead-out 305 area is located at the outer radius of the disc. This layout structure is comparable with the layout of the single layer 320 disc. Reading of the data is done, as in a DVD-5, 200 from the inner radius of the disc to the outer radius, for both layers. With proper authoring of the content on the disc, the PTP method can allow quick access from layer to layer, for example in order to provide background information and commentary in one track along with the movie in the other track.

[0128] A dual-layer Opposite Track Path (OTP) 325 disc, also illustrated in Figure 6, offers the possibility of seamless continuation of the playback from the L0 100 to the L1 115 layer. The first information layer (L0) 100 starts with a lead-in area at the inner radius of the disc and ends with a so-called middle area 330 at the outer radius. The second information layer starts with a Middle Area 330 at the outer radius and ends with a lead-out 300 area at the inner radius of the disc. Reading the data 335 stored on the disc will start at the inner radius of the first information layer and proceed until the Middle Area 330 of this layer is reached. Then a switch over to the Middle Area in the second information layer is made, in order to continue reading of the data from the outer radius up to the lead-out 305 Area in the inner radius of the second layer (L1) 115.

[0129] *Single layer optical discs* One embodiment of the present invention is an optical disc similar to a DVD-5 where, unlike a standard DVD-5, the interstitial layer 400 typically used as the bonding layer 401 is in the optical path 405 of the reading laser (e.g., see Figure 7). In one embodiment of the present invention (labeled below as "Special DVD-5 design #1"), this disc is manufactured by inverting the reflective layer 410 of a standard DVD-5, and reading the information through the non-information-bearing substrate 415 and the bonding layer 401. In another embodiment of the present invention (labeled below as "Special DVD-5 design #2"), the direction of the spiral track is inverted during mastering, the information bearing substrate is flipped "upside down", and the information is read through the non-information bearing substrate 415 and the bonding layer 401. In this type of optical disc, the bonding

layer 401 is an integral part of the optical path 405 of the reading laser. Even though the structure of the "Special DVD-5" disc described herein differs from a standard DVD-5, a player would play this disc as if it were a standard DVD-5.

[0130] This embodiment of the present invention has significant advantages in terms of allowing the manufacturing of a low-cost "limited-play" optical disc that is resistant to attempts to defeat it. In particular, because it does not incorporate any additional layers compared to a standard DVD-5, it can be manufactured on equipment designed to manufacture DVD-5 discs with minimal changes to that equipment. Furthermore, because the bonding layer 401 is in the optical path, 405 modifying that layer to interfere with the reading of data in response to a predetermined stimulus results in a disc that is very difficult to defeat, as the interfering layer 400 is protected by the two substrates 415 and 420, respectively of the optical disc. For example, grinding the interfering layer 400 off the disc is impractical, as it would most likely destroy the disc. Similarly, attempting to compromise the bonding/interfering layer in other ways is likely to destroy the structural integrity of the optical disc.

[0131] We now describe in detail the manufacturing of three embodiments of the current invention, which we label as "Special DVD-5" designs 1, 2 and 3.

[0132] *Special DVD-5 design #1* In one embodiment of the invention, the above process is modified by using the mother stamper to replicate the L1 disc substrate 420. Figure 3 shows how the stamper or father is used to mold a normal single layer DVD-5 substrate. Figure 8 illustrates manufacturing this embodiment of the current invention by using the mother stamper 40 and creating a disc with the bonding layer 401 in the optical path 405.

[0133] In a normally molded standard DVD-5 information is encoded on the L0 100 side with "pits" 20 and "lands" 25 molded on the L0 substrate 100 and metallized with a reflective metal coating, 105 as illustrated in Figure 2, Figure 3 and Figure 9. In one embodiment of the current invention, the mother stamper 40 is used to mold the L1 side 420 as shown in Figure 8. This side is subsequently metallized and bonded with a blank L0 substrate, 415 leaving the bonding layer 401 in the optical path, 405 as shown in Figure 10. Using the specified layer thickness of 0.055 mm +/- 0.015, the thickness of the L0 substrate 100 is targeted at 0.55 mm ~ 0.57 during molding, to

yield a focal length of the disc thickness (including the bonding layer) consistent with standard DVD specifications, allowing the player to be in the normal focusing range for reading a L0 layer 100. Thus the player interprets the disc as a standard single layer DVD-5. Field experience has shown that spacer layer thickness can be maintained at 0.045 ~ 0.065 mm consistently in production. This controlled variation in production along with the reduced thickness of the molded disc keeps the focus and optics within the specifications set by the DVD licensing authority and the hardware manufacturers.

[0134] For the replication facility, most applications would remain unchanged in the actual pressing and bonding portions of production. The main areas of change would be in the LBR (laser beam recording) and developing areas of mastering. Typically, masters are cut with larger pit volumes to compensate for plastic shrinkage and replication inefficiencies. The ratio of pit to land areas on a disc is measured by a term called asymmetry. Because asymmetry is a ratio of pit to land area, and because for each pit area, typically defined by I3 to I14 pit, there is an equal and opposite land area I3 to I14 land, typically it is easier for manufacturers to target a positive asymmetry (larger pit area) to account for losses in replication to the plastic substrate. For example, the master may be cut with a positive 10~12 % for asymmetry, while the end result from molding may be 5~7 %. The specification for the disc substrate is: $-0.05 < \text{asymmetry} < +0.15$. In the case of DVD discs, a positive asymmetry represents a larger pit volume compared with the land area.

[0135] For this embodiment of the invention, it may be desirable to change the asymmetry set point on the LBR to produce a higher asymmetry value on the father stamper while subsequently increasing the asymmetry on the mother stamper used for molding. Asymmetry can be changed on the master by modifying the power of exposure, focusing intensity and offset, developing time/ endpoint detection, or baseline (control of how fast the laser diode cuts the laser exposure beam off between exposure). There are many other possible ways to control asymmetry, but the basic process or set point control would be the easiest to implement. This process of molding from the mother stamper would also eliminate the need to grow additional stampers and the subsequent yield losses attributed to the family process.

[0136] In this embodiment of the invention, the pits 20 are molded in the L1 layer 420 using a mother stamper, 40 and as a result the surface of the pits 20 is elevated relative to the reference plane 450 of the L1 layer 420 as illustrated in Figure 10. This reference plane 450 is typically used for tracking by the disc player (tracking area). By contrast, in a normal DVD-5 the pits 20 are molded as cavities in the L0 substrate 100 as illustrated in Figure 9. Using the common convention of describing a disc as if it is in a play position where it is read from the bottom, and a convention that we will follow hereinafter unless otherwise specified, in a normal DVD-5 the pits 20 are lower than the reference plane 450, while the lands 25 are at the reference plane 450 (see Figure 9). In the embodiment of the invention described above the blank L0 substrate 415 and the bonding layer 401 are below the L1 substrate 420 in the optical path 405 of the reading laser, and the surface of the pits 20 in the L1 substrate 420 is below the reference plane 450 while the lands 25 are at the reference plane 450 (see Figure 10). Note that this construction requires the pits 25 to be molded in an unconventional way (they protrude from the reference plane 450 of the disc), which is achieved by molding the L1 substrate 420 from a mother stamper 40. Figure 11 shows an Atomic Force Microscope (AFM) image of a Father stamper 30 for a DVD-5, Figure 12 shows an AFM image of the corresponding Mother stamper 40, and Figure 13 shows an AFM image of the L1 layer of a Special DVD-5 Design #1, molded from the Mother stamper 40.

[0137] This molding required for this embodiment of the invention can present certain challenges. In a typical injection molding process, the polymer material flows around the pits 20 on the stamper, which are raised from the reference plane 450. This is easier than to mold from the mother, where the polymer material must flow into cavities that will form the pits 20 on the separated part. As the material flows over the surface of the mother stamper 40, the molecular chains cool off through contact with the relatively colder reference surface of the stamper. After the mold is completely filled, then pressure must be applied to bend and force the cooler polymer material into the pit 20 cavities. Although this method is capable to reproduce discs within the specifications of a standard DVD-5 configuration, the molding process is more difficult. However, one skilled in the art can address such challenges by adjusting the process characteristics of the molding machine, e.g., by increasing mold surface

temperature and cycle time. Alternatively appropriate materials with higher melt flow rate could be used, such as PMMA or high melt flow rate polycarbonate. For example, General Electric's SPOQ research grade polycarbonate has twice the melt flow rate of standard grade polycarbonate.

[0138] As long as the index of refraction (RI) of the bonding adhesive used is approximately equal to the RI of the L0 substrate 415, the thickness of the bonding layer 401 is uniform, and the thickness of the L0 substrate 415 has been adjusted to compensate for the presence of the bonding layer 401 in the optical path 405 of the reading layer, the player will not be able to distinguish Special DVD-5 Design #1 from a standard DVD-5. Experience has shown that playable discs can be manufactured even without these adjustments, because most players will play discs that do not fully conform to the DVD specification, as long as the departure from the specification is not excessive.

[0139] *Example 1: Special DVD-5 Design #1* A father stamper 30 was mastered with slightly increased symmetry (positive asymmetry = larger pits 20 compared to lands 25). The asymmetry can be increased or decreased many ways. The simplest method and the one used for this design, was to increase the development time (endpoint detection set point) to overdevelop the pits 20. By lengthening the development process, the pit volume surrounding, that which was exposed, will increase in volume causing a shift to positive asymmetry.

[0140] A mother stamper 40 was grown from the father stamper 30 as with a normal family process. Disc substrates were molded from the mother stamper 40, taking advantage of the larger indentation caused by the positive asymmetry. The larger pits 20 that resulted from molding with the mother 40 helped to compensate for the additional shrinkage of the pit 20, which is now an extremity to the body of the substrate, rather than a cavity as in the standard molding process. Typically, the molten plastic flows around the pits 20 in a normal (father 30 or son 45) stamper like a river flows around a hill. As the level rises, the hill or the pit 20 will be covered. As the molten plastic flows across the cooler stamper surface, a skin layer forms right on the surface that acts as a heat insulator. This allows for the plastic to maintain its flow rate necessary to form the pit volume without undue stress or cooling. In the case of

Special DVD-5 design #1, the plastic has to flow into the indentations of the mother stamper 40, rather than around the bumps of a father/son stamper 30 and 45 respectively. This is difficult because as the plastic flows across the surface of the mother stamper 40, it again forms a skin layer on the surface. Then as the mold volume increases with continued injection and packing/holding time, the molten plastic must be forced into the indentation. Because this skin layer is solidified typically below the glass transitional temperature of the plastic, the material does not free flow into the indentation. Because the pit-forming plastic in the L1 substrate 420 of Special DVD-5 design #1 is not in the optical path of the reading laser, the material can be filled with greater force without the concern for birefringence and residual stress, although there is a limit to the pressure due to warping (tilt) caused by excessive packing pressure on the plastic. In this example, the combination of larger indentations in the mother stamper 40 as well as increased mold temperatures assisted in replicating the desired pits 20. Typically, in direct water injection systems for the mold heating and cooling, safety interlocks of 120 ° C max temperature limit the temperature of the water. By using a 50 / 50 solution of glycol and water, the temperature can be effectively run at a max temperature of 130 ° C. This added temperature assists in keeping the skin layer in the molten state, close to its glass transition temperature, which facilitates the replication of L1 substrates 420 for Special DVD-5 design #1. Also, the mother stamper 40 must be filled quickly with molten plastic in order to prevent skinning on the surface.

[0141] L1 substrates 420 were molded as above using a mother stamper 40. Figure 13 shows an Atomic Force Microscope (AFM) image of an L1 layer 420 molded from a mother stamper 40. Figures 11 and 12 show AFM images of the father 30 and mother 40 stampers used in the process. For these discs to be formed, it was necessary to raise the melt temperature from 360 ° C to 390 ° C while maintaining a mold temperature of 121 ° C compared to the standard of around 100 ° C. The clamp force was set at maximum of 30 tons and the filling time was decreased from 0.13 to 0.09 seconds. These parameters were adjusted until the proper pit 20 formations were achieved.

[0142] The molded L1 substrates 420 were bonded using optical grade UV curable DVD adhesives, as used in DVD-9 production, to blank L0 substrates 415, to manufacture

design #1 of the Special DVD-5. L0 substrates 415 were molded at a thickness of 0.55~0.57 mm (i.e., 30~50 micron thinner than standard DVD halves) to compensate for the bonding layer in the optical path, thus preserving the same focal depth for the information-carrying layer as in a standard DVD-5.

[0143] *Special DVD-5 design #2* The electronics of optical media drives, including DVD players, are typically designed to read the information contained in a layer on the disc by identifying the interference patterns caused by the transitions from a "land" 25 to a "pit" 20 in that layer. The pits 20 are often molded with a height approximately equal to, and typically somewhat less than, one quarter of the wavelength of the reading laser. For example, in DVDs the typical wavelength of the reading laser is 635~650 nanometers (in vacuum), or 410~420 nm in a material with RI = 1.55 (which is typical of the materials used to manufacture the DVD substrates), and thus the height of the pits 20 in a standard DVD-5 should be approximately 100~105 nanometers. Consequently, a transition from a land 25 to a pit 20 or vice versa corresponds to a change to the path of the reading laser of approximately one half wavelength, or a phase change of approximately 180 degrees. Two identical waves with a phase difference of 180 degrees will interfere with each other and cancel out, and the electronics of the optical drive are designed to detect the resulting interference patterns. Using the standard convention of the disc being read from below, in a standard DVD-5 the surface of the pits 20 is below the surface of the land 25, and a transition from a land 25 to a pit 20 is a "down" transition, while a transition from a pit 20 to a land 25 is an "up" transition. If the height of the pits 20 is one quarter of the wavelength of the reading laser then a transition from a land 25 to a pit 20 in a standard DVD-5 is a "down" transition that corresponds to a phase change of +180 degrees, and a transition from a pit to a land 25 is an "up" transition that corresponds to a phase change of 180 degrees. If an "up" and a "down" transition differ by 360 degrees, as in the case described above, their effects will be identical. One implication of this is that the pits 20 of a DVD-5 could be molded in the opposite direction, i.e., with the pit surface approximately one quarter wavelength above the land 25 surface, and the electronics of the optical disc player are unlikely to be influenced by whether detected transition is in the "up" or "down" direction, i.e. whether a pit 20 area is higher or lower than the land 25 area.

[0144] In a standard DVD-5, the laser pick up will read through the L0 substrate 100 focusing on the pits 20 aligned in a spiral track. The rotation of the disc would be in the counterclockwise direction (as seen from the side of the reading laser), and the spiral track would be in the clockwise direction. Given that the pit 20 direction can be reversed without changing the electrical signal seen by the player, in another embodiment of the current invention the pits 20 are molded as depressions 500 into the L1 substrate 420, by employing a normal (father/son) DVD-5 stamper 30/45, as illustrated in Figure 14. The direction of the spiral track is reversed during mastering, as the disc will be read from the side of the bonding layer 401, rather than through the substrate as in a standard DVD-5. The resulting disc has information encoded as a DVD-5, although the pits 20 are formed in the L1 layer 420: the surfaces of the pits 20 are above the surfaces of the lands 25, and the lands 25 are at the reference plane of the L1 layer 420, as illustrated in Figure 15. The pit 20 width, length, height, and shape give the corresponding HF signals needed to decode the data on the DVD. The signals are encoded utilizing an eight-to-fourteen modulation (EFM) signal. The pit 20 edges and slopes of the sidewalls serve to distinguish the logical transition of 0's and 1's. This results in pit 20 length units measured as 3 units long to 14 units long, which set the frequency limits of the EFM signal, read from the disc. This measurement is commonly referred to as 3T - 14T signal with T referring to a period of time. As long as the pits 20 are replicated in standard fashion, the player will still be able to distinguish the pit 20 start and end position, while reading from the reverse side, to correctly identify its data identity. In many circumstances this will be the preferred embodiment of the invention, as it does not require molding from the mother stamper 40, as is the case with Special DVD-5 design #1 above.

[0145] The actual height of the pits 20 in a standard DVD-5 is typically somewhat less than one quarter wavelength of the reading laser. This is intended to avoid complete cancellation of the reflected laser during a pit-to-land transition, which facilitates the functioning of player electronics. For example, a value of $0.88 \times (\text{laser wavelength}) / 4$ is sometimes recommended, i.e. approximately 90 nanometers for a material with RI = 1.55. Thus it may be desirable to mold the pit 20 surfaces in this embodiment of the current invention somewhat higher than one quarter the wavelength of the reading laser, so that the change in the path of the reading laser during a transition from a

land 25 to a pit 20 in the special DVD-5 design #2 will be exactly one wavelength longer than the corresponding change in a standard DVD-5. For example, if the reading laser wavelength is 650 nanometers (i.e., 420 nm in a polycarbonate substrate of $RI = 1.55$), and the pits in a standard DVD-5 are 90 nanometers, the pits 20 in this embodiment (Special DVD-5 design #2) can be molded at 120 nanometers, i.e., one half wavelength (210 nm) from the position of the pit 20 surface in design #1.

[0146] *Example 2: Special DVD-5 Design #2* A special stamper for molding L1 substrates 420 for Special DVD-5 Design #2 was produced through a modified mastering process, where the direction of rotation of the laser beam recorder turntable was reversed during the cutting process, resulting in a spiral tracking path in the opposite direction from that in a normal DVD-5. This stamper was produced by forcing the turntable to rotate in the reverse direction from cutting a normal DVD-5, while the content information was fed to the laser beam recorder as a DVD-5 image. The scanning velocity that is normally preset for DVD formats was manually set to the velocity of 3.49 m/s typical in DVD-5 mastering. L1 substrates 420 were then molded on standard molding machines set up for DVD-5 fabrication.

[0147] Some of the molded L1 substrates 420 were bonded using optical grade UV curable DVD adhesives to blank L0 substrates 415, to manufacture design #2 of the Special DVD-5. As in Example 1, the L0 substrates 415 were molded at a thickness of 0.55~0.57 mm (i.e., 30~50 micron thinner than standard DVD halves) to compensate for the bonding layer 401 in the optical path, thus preserving the same focal depth for the information-carrying layer as in a standard DVD-5. To bond the discs, the machines were placed into a DVD-9 production mode and the semi-reflective metallizer for the L0 layer was taken offline. Then the cure time was adjusted to compensate for the decrease in cure exposure needed due to the missing semi-reflective layer. Curing was basically set for a DVD-5 disc, and the disc was flipped to cure through the L0 layer. This function is typically reserved for DVD-9 production.

[0148] The discs were then tested with a Koch DVD testing system and played in four different DVD players. They performed indistinguishably from regular DVD-5 discs, as illustrated in Figures 21 and 22. Also, the discs played with no errors in an additional three DVD players and two DVD-ROM drives.

[0149] Some of the molded substrates were used to manufacture discs with a reactive bonding layer (see Example 9). *Special DVD-5 design #3* The electronics of optical media drives, including DVD players, can be designed to read the information contained in a layer on the disc by identifying pits 20 and lands 25 in that layer based on the absolute and/or relative elevation of these pits 20 and lands 25, thus distinguishing between an "up" and a "down" transition in the information encoding layer, but without being influenced by the elevation of the pits 20 and lands 25 relative to the reference plane 450 of the layer. Thus in another embodiment of the current invention, during mastering the direction of the spiral track is reversed and also the pits 20 and lands 25 are reversed, so that the pits 20 become lands 25 on the resulting stamper 30, and lands 25 become pits 555. The L1 substrate 420 is then molded by employing 550 a normal (father) stamper 30 and is bonded to a blank L0 substrate 415. The resulting disc has information encoded as a DVD-5, the relative elevation of pits and lands, and the "up" and "down" transitions in the information encoding layer, are identical to a DVD-5. Specifically, the surface of the pits is below the surface of the lands. However, while in a standard DVD-5 the surface of the lands is at the reference plane of the L0 layer, in this embodiment it is the surface of the lands 560 (corresponding to pits on a standard DVD-5) that is at the reference plane of the L1 layer, with the pits 565 (corresponding to lands on a regular DVD-5) being above this reference plane, as illustrated in Figure 16.

[0150] *The reactive bonding layer* Another embodiment of the present invention is having a reactive material incorporated in an interstitial layer. In one embodiment, the interstitial layer is the bonding layer of the disc.

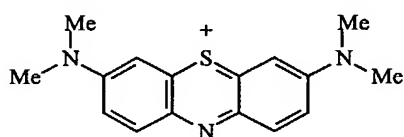
[0151] In one embodiment of the invention, the stimulus triggering the reaction is exposure to atmospheric oxygen. Upon exposure to oxygen, a reactive material, e.g., leuco methylene blue, which is essentially colorless, is oxidized to form an opaque or semi-opaque layer (e.g., the deep blue dye, methylene blue). Data storage media with the opaque/semi-opaque layer can no longer be played in media players. By adjusting the time it takes to turn opaque, this method can be used to provide limited-play data storage media having the desired life for the given application.

[0152] The reactive layer, which comprises both a carrier and a reactive material, should

initially have sufficient transmission to enable data retrieval by the data storage media device, and subsequently form a layer which inhibits data retrieval by that device (e.g., which absorbs a sufficient amount of light i.e., incident and/or reflected light) at the wavelength of the laser in the given device). Typically a layer that allows an initial percent reflectivity from the reflective layer of about 50% or greater can be employed, with an initial percent reflectivity of about 65% or greater preferred, and an initial percent reflection of about 75% or greater more preferred. Once the media has been exposed to oxygen, e.g., air, for a desired period of time (e.g., the desired allowable play time of the media), the layer preferably comprises a percent reflectivity of about 45% or less, with about 30% or less preferred, about 20% or less more preferred, and about 15% or less especially preferred.

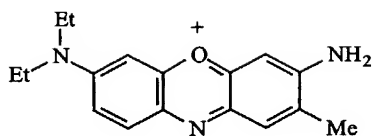
[0153]

Possible reactive materials include oxygen sensitive leuco or reduced forms of Methylene Blue, Brilliant Cresyl Blue, Basic Blue 3, Methylene Green, Taylor's Blue, Meldola's Blue, New Methylene Blue, Thionin, Nile Blue, Celestine Blue, and Toluidine O, as well as reaction products and combinations comprising at least one of the foregoing material; the structures of which are set forth below:

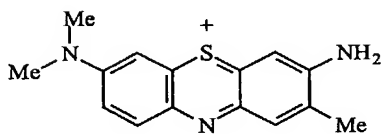


Methylene Blue

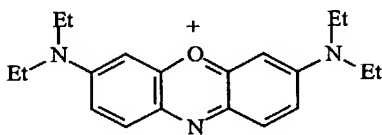
661nm



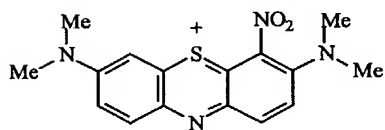
Brilliant Cresyl Blue 622 nm



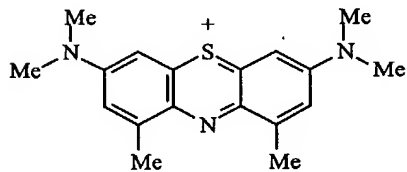
Toluidine Blue O 626 nm



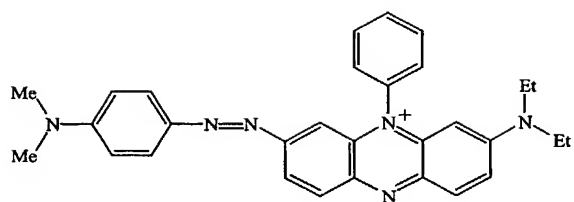
Basic Blue 3 654 nm



Methylene Green 657, 618 nm

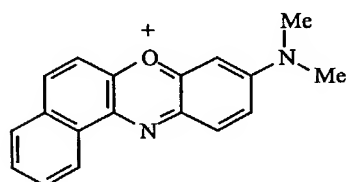


Taylor's Blue 649 nm



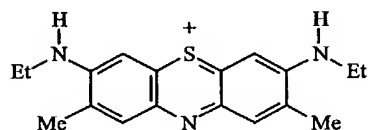
Janus Green B

660, 395 nm



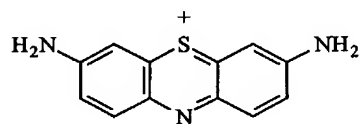
Meldola's Blue

570 nm



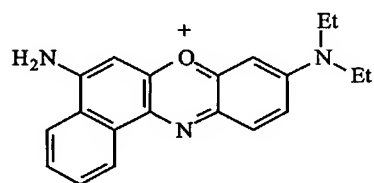
New Methylene Blue

630, 591 nm



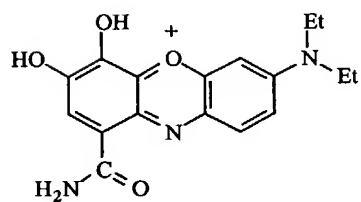
Thionin

598 nm



Nile Blue

638 nm



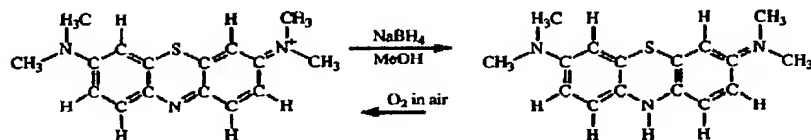
Celestine Blue

642 nm

[0154]

A method of synthesis of leucomethylene blue and the oxygen dependent

reoxidation to form the colored form of the methylene blue dye is shown below:



[0155] In addition to the above reactive materials, numerous other dyes and light blocking materials, can be synthesized to operate to render the data storage media limited play. For example, some other possible reactive materials can be found in U.S. Patent No. 4,404,257, hereafter incorporated by reference, and U.S. Patent No. 5,815,484, hereafter incorporated by reference. The reactive materials can further comprise a mixture comprising at least one of any of the above mentioned reactive materials.

[0156] The reactive material is preferably mixed with a carrier for deposition on and/or impregnation into at least a portion of the surface of the substrate. Possible carriers comprise the thermoplastic acrylic polymers, polyester resins, epoxy resins, polythiolenes, UV curable organic resins, polyurethanes, thermosettable acrylic polymers, alkyds, vinyl resins and the like, as well as combinations comprising at least one of the foregoing carriers. Polyesters include, for example the reaction products of aliphatic dicarboxylic acids including, e.g., fumaric or maleic acid with glycols, such as ethyleneglycol, propyleneglycol, neopentylglycol, and the like, as well as reaction products and mixtures comprising at least one of the foregoing.

[0157] Some epoxy resins, which can be the used as the organic resin, include monomeric, dimeric, oligomeric, or polymeric epoxy material containing one or a plurality of epoxy functional groups. For example, reaction products of bis phenol-A and epichlorohydrin, or the epichlorohydrin with phenol-formaldehyde resins, and the like. Other organic resins can be in the form of mixtures of polyolefin and polythiols, such as shown by Kehr et al, U.S. Patent Nos. 3,697,395 and 3,697,402, hereafter incorporated by reference.

[0158] *A non-bonding reactive layer* Optionally, the reactive layer can be applied to the substrate using various coating techniques such as painting, dipping, spraying, spin coating, screen printing, and the like. For example, the reactive layer can be mixed

with a relatively volatile solvent, preferably an organic solvent, which is substantially inert towards the polycarbonate, i.e., will not attack and adversely affect the polycarbonate, but which is capable of dissolving the carrier. Examples of some suitable organic solvents include ethylene glycol diacetate, butoxyethanol, the lower alkanols, and the like.

[0159] For surface coatings, the reactive layer may also optionally contain various additives such as flatting agents, surface active agents, thixotropic agents, and the like, and reaction products and combinations comprising at least one of the foregoing additives. The thickness of the reactive layer is dependent upon the particular reactive material employed, the concentration thereof in the reactive layer, and the desired absorption characteristics of the layer both initially and after a desired period of time.

[0160] *Development of blocked reactive compounds* One embodiment of the present invention is the use of blocked forms of the reactive compounds in the reactive layer. These compounds will unblock within a predetermined time period after the disc is manufactured or packaged, and typically before the disc is used by the consumer. This is desirable when the stimulus that triggers the reaction that causes the disc to become unplayable (e.g., atmospheric oxygen) can trigger this reaction during the manufacturing of the disc, and thus measures need to be taken so that the reactive compound is not activated during the manufacturing of the disc. For example, in the case of oxygen triggered reactions, unless a blocked form of the reactive compound is used, manufacturing may need to take place in an oxygen free environment, such as a nitrogen atmosphere.

[0161] One embodiment of the present invention comprises the idea of using a chemically blocked reactive substance for the purpose of producing optical discs that become unplayable after being exposed to oxygen, a specific such blocked leuco dye, a method of preparing this leuco dye precursor, a formulation including this leuco dye precursor which permits the deblocking and oxidation of the leuco dye precursor at acceptable rates, methods of applying this formulation to optical discs both on the surface of optical discs and as bonding layers for optical discs, the use of bases to increase the rate of methylene blue generation in blocked leuco dye-containing layers in or on optical discs, and the use of silylating agents such as hexamethyldisilazane

to stabilize the blocked leuco dye in coating fluids.

[0162] In one embodiment of the invention, to manufacture an optical disc that becomes unplayable after being removed from its package (a "limited-play disc"), the disc incorporates a reactive layer with a composition containing a leuco dye which oxidizes to a colored dye which absorbs light at the wavelength of the reading laser of an optical disc player, preventing enough of the reading laser light from being reflected off the disc to render the disc unplayable. The oxidation of the leuco dye can be initiated by exposure of the coating containing the dye to atmospheric oxygen, which diffuses through the coating to oxidize the leuco dye molecules. One problem with putting such a coating on the surface of the disc is the possibility of the coating being removed by a consumer to make the disc permanently playable. Another problem with putting such a coating on the surface of an optical disc is that this requires an additional step in the disc manufacturing process, entailing higher cost, special tooling for production equipment, and inevitably lower manufacturing yields. Finally, the oxygen-sensitive fluid used to make such a coating is difficult to handle because of its oxygen sensitivity.

[0163] In some methods of coating a leuco-dye-containing fluid on the surface of an optical disc, some of which were described above, the coating is solvent based and the solvent must evaporate to yield a hard coat containing the leuco dye and any other components required, typically bound in a polymer matrix. There are several disadvantages to such a solvent coating. First, most of the solvent based fluid is spun off of the disc during a spin coating manufacturing process and is difficult or impossible to recover due to solvent evaporation, which both wastes fluid (increasing the cost of the process) and fouls the coating equipment. Second, evaporation of the solvent takes time, which reduces the rate at which such coated discs can be manufactured and thereby increases the cost of the process. Third, the solvent vapors emitted by the coated disc during the coating and drying process must be vented from the manufacturing equipment, increasing the cost of the installed equipment presenting process and environmental obstacles to disc replicators considering adopting this manufacturing process.

[0164] All of the problems discussed in the previous two paragraphs could be avoided if

the leuco dye could be coated in a solventless, light or radiation cured (hereafter called generically "UV-cured") layer, and if this layer could be the same as the optical disc bonding layer that is used to bond the two substrates which compose certain types of optical disc, such as a DVD. The major obstacle to creating such a system is that many leuco dyes, and in particular leucomethylene blue (hereafter "LMB", which has been used by the present inventors to render DVDs unplayable in a solvent-based, surface coated system), inhibit both radical and cationic polymerization reactions of the type used to cure UV-curable monomers such as the acrylates that are commonly used as adhesives for bonding DVD substrates. The oxidized dyes (including methylene blue) also are inhibitors of such polymerization reactions. So putting a leuco dye (which will inevitably contain some of the oxidized, colored dye) in a UV-curable composition will either prevent the UV-curing from taking place, or slow the UV-curing and make the process much less economical by reducing the rate at which discs can be manufactured. Moreover, the process of UV-curing can result in some of the leuco dye becoming oxidized if any oxygen or other oxidizing agent is present in the layer to be cured, resulting in a product prematurely containing oxidized dye which may interfere with the readability of the disc or change the rate at which it becomes unreadable after exposure to oxygen.

[0165] Chemically blocked (sometimes called "protected") leuco dyes (also called "leuco dye precursors") are known and have been used for decades in applications such as "carbonless copy paper". In particular, blocked versions of leucomethylene blue are known and have been used in such applications, and one such compound at least, benzoyl-leucomethylene blue (BLMB), is commercially available. However, we have found that BLMB does not deblock easily enough to yield an acceptable limited play DVD product. Other blocked leucomethylene blue compounds share this problem, or deblock too easily such that oxidizable leucomethylene blue is generated in the coating fluid before it is desired.

[0166] We have found that triisopropylsilyloxycarbonylleucomethylene blue (hereafter "TIPSOCLMB"), whose structure and exemplary synthesis are illustrated in Figure 17 and described in Example 4, has the following desirable properties for use in creating limited-play DVDs: 1. It is readily synthesized in two steps from commercially available starting materials. By isolating and purifying the BOC-LMB produced in the first step

as shown in Figure 17, the TIPSOCLMB is prepared from a pure compound rather than from the typically very impure methylene blue.

[0167] 2.It can be incorporated into an acrylate formulation described in Example 5 in which it is stable (to conversion to oxidized methylene blue) for at least several weeks at temperatures below 0 C, allowing coating formulations to be prepared at one facility and shipped to another facility for DVD manufacturing if desired.

[0168] 3.It can be deblocked in a period of a week or less, presumably by a hydrolysis reaction involving water or other nucleophiles which can either be provided in the acrylate formulation or be absorbed from the atmosphere in which the DVD is manufactured or in the DVD packaging material.

[0169] 4.The deblocked LMB is stable (to oxidation to methylene blue) in the absence of oxygen. The rate at which the deblocked LMB oxidizes in the presence of oxygen can be controlled by controlling the effective pH of the coating formulation. It is known in the art that the rate of oxidation of LMB increases as the pH of its environment increases. Thus the rate of oxidation can be increased by the addition of basic substances that are soluble in the matrix containing deblocked or blocked LMB and which do not react with the matrix or substrate used. One such basic compound is DABCO (1,4-diazabicyclo[2.2.2] octane), an amine. Other amines may be added or substituted. Further, the addition of a strong protic acid such as camphorsulfonic acid decreases the rate of LMB oxidation in a polymer film.

[0170] 5.In the absence of water or other nucleophiles, it is a stable solid which can be stored after synthesis for at least several months, even in the presence of oxygen. Acrylate-based coating fluids containing TIPSOCLMB can be handled in the presence of oxygen until the deblocking reaction has taken place, which reaction is slow enough that the handling of the coating fluid during the DVD manufacturing process can be done in normal (undried) air and is not difficult.

[0171]

Example 3: BocLMB Preparation

[t5]

<i>Chemical</i>	<i>Amount</i>	<i>Moles</i>	<i>Mol. Wt.</i>
Na ₂ S ₂ O ₄	60.0 g	0.345 (2.1 eq)	174.11
H ₂ O	300 mL		
10% aq. NaOH	240 mL		
Methylene Blue	60.0 g	0.160	373.90
CH ₂ Cl ₂	700 mL + 25 mL		
Boc ₂ O	81 mL (d = 0.95 g/mL)	0.352 (2.2 eq)	218.25
DMAP	3.0 g	0.025 (0.15 eq)	122.17
Hexanes	400 mL		
Methanol	200 mL estimate		

[0172] In a 2-liter separatory funnel was dissolved 60.0 g of sodium hydrosulfite (sodium dithionite, Na₂S₂O₄) in 300 mL cold distilled water. To this solution was added 60.0 g methylene blue (dark green powder) from several different bottles, and the separatory funnel was stoppered and shaken vigorously over a 30-minute period, during which time the dark green solids gradually form a tan suspension of insoluble leucomethylene blue. To this suspension was added three 60-mL portions of 10% aqueous sodium hydroxide solution with vigorous shaking after each addition. Some heat is evolved, and a lighter suspension results. After allowing the mixture to stand for a short while to cool, 700 mL methylene chloride was added and the separatory funnel was stoppered and shaken to dissolve the solids. An amber organic layer began to separate below an emulsion. An additional portion of 60 mL aqueous NaOH was added, the stoppered funnel was shaken, and the emulsion was allowed to stand for 30 - 60 minutes to separate into two liquid phases. Alternatively, fresh Na₂S₂O₄ and reasonably pure methylene blue may be used to result in a faster and cleaner phase separation.

[0173] To a 1-liter, 3-necked, round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet inside a fluted adapter (Aldrich Z11,563-0) packed with 1.5 sheets of crumpled small Kimwipe tissues (11 X 21 cm) was added 81.0 mL di- *tert* - butyldicarbonate (Boc₂O) diluted with 25 mL methylene chloride. After stirring under nitrogen for 5-10 minutes, 3.0 g of 4-(dimethylamino)pyridine (DMAP) was added followed by dropwise addition of the leucomethylene blue solution from the separatory funnel and through the fluted Kimwipe-containing tube. The stem of the

separatory funnel was connected to the fluted tube through a one-holed rubber stopper so that the addition was performed under nitrogen. Gas evolution (CO₂) began immediately. After two hours, the addition was completed to give a dusty green reaction mixture that was stirred overnight under nitrogen at room temperature.

[0174] On the following morning, the dusty green reaction mixture was arranged for atmospheric distillation. About 550 mL CH₂Cl₂ was distilled off and replaced with 300 mL hexanes. A gray-blue solid separated out. Distillation was continued until the head temperature reached about 55 ° C. The mixture was allowed to cool; then the solid was collected by filtration through a sintered glass funnel. The solid was washed with hexanes (2 X 50 mL) to remove excess Boc₂O, and then it was washed with methanol (amount unspecified, 4 X 50 mL estimate) to remove unreacted and oxidized leucomethylene blue until the wash liquid was only faintly blue. The resulting gray solid was dried in air and then under vacuum at room temperature. Yield: 47.0 g (76%). (MW of BocLMB = 385.53) Thin layer chromatography analysis on a 5 X 10 cm Whatman K5F silica gel plate eluting with 5% acetone in methylene chloride showed a faint blue spot at the origin, a very weak spot at R_f = 0.58, and a large product spot at R_f = 0.63. The initially colorless product spot became dark blue upon standing in air, and rapidly when heated in a 120 ° C oven.

[0175] Repetition of this reaction at the same scale resulted in a yield of 48.0 g (78%).

[0176] *Example 4: TipsocLMB Preparation*

[0177]

[t7]

<i>Chemical</i>	<i>Amount</i>	<i>Moles</i>	<i>Mol. Wt.</i>
BocLMB	35.61 g	0.092	385.53
CH ₂ Cl ₂	200 mL		
2,6-Lutidine	26.0 mL (d = 0.92 g/mL)	0.223 (2.5 eq)	107.16
TipsOTf	39.0 mL (d = 1.14 g/mL)	0.145 (1.5 eq)	306.42
Hexanes	420 mL		

[0178] To a 500-mL, 3-necked, round-bottomed flask equipped with a magnetic stirrer, addition funnel, and condenser under a nitrogen bubbler was dissolved 35.61 g BocLMB in 200 mL methylene chloride to give a blue solution. To this solution was

added 26.0 mL 2,6-lutidine followed by dropwise addition of 39.0 mL of triisopropylsilyl trifluoromethanesulfonate (TfOTf) over a 15 minute time period. The green-blue reaction mixture was then stirred under reflux for 6 hours. TLC analysis (K5F silica, 5% acetone/CH₂Cl₂) showed only a small amount of BocLMB starting material present at R_f = 0.67 with a large product spot at R_f = 0.74. The reaction mixture was then stirred overnight at room temperature under nitrogen.

[0179] On the next morning, the green-blue clear reaction mixture was again stirred under reflux for one hour. TLC analysis still indicated that a trace of BocLMB or similar R_f impurity was present. The solution was then concentrated on a rotary evaporator under vacuum to remove most of the methylene chloride, resulting in a dark green-blue syrup. After addition of 200 mL hexanes, the mixture was stirred by hand to effect the separation of a blue-gray solid. Upon heating this mixture under reflux with continued hand stirring, the TipsocLMB product dissolved in the hot hexanes leaving behind a dark blue salt residue as a melt or crusty solid. The hot hexanes solution was decanted from the residue, and the residue was further extracted with 60 mL boiling hexanes. The combined hot hexanes extract (green in color) was allowed to cool slightly and was then filtered through a 1.5 cm-thick layer of Celite to obtain a clear, pale tan filtrate. After washing the Celite twice with 30 mL portions of hot hexanes, the combined filtrate (~320 mL volume) was placed in the freezer (about -20 °C) overnight.

[0180] On the following morning, an off-white solid with a greenish cast was observed to have crystallized. The mixture was filtered cold, and the product was washed with cold hexanes (2 X 50 mL), sucked dry, and dried under vacuum at room temperature to an off-white solid. Yield: 33.3 g (75%). (MW of TipsocLMB = 485.77) The melting point from an earlier run was 121-123 °C.

[0181] TLC analysis (K5F silica, 3% acetone/CH₂Cl₂) showed very weak spots at the origin and at R_f = 0.53 (probably unreacted BocLMB) with the main spot at R_f = 0.61 that is initially colorless and becomes dark blue upon standing at room temperature for several hours, or in a 120 °C oven for a few minutes.

[0182] Examples 5 and 6 illustrate how TIPSOCLMB can be incorporated in a coating fluid that can be UV-cured to create a reactive layer containing TIPSOCLMB. Example 7

illustrates how the above technique can produce an interstitial reactive layer, which allows the Special DVD-5 designs 1, 2 and 3 to be used to manufacture expiring optical discs. Example 8 illustrates how TIPSOCLMB deblocks and becomes oxygen sensitive LMB in either a surface or an interstitial layer. When exposed to oxygen, the LMB oxidizes into methylene blue, as illustrated by the increasing cyan density in Figure 18; methylene blue strongly absorbs light in the 650nm wavelength, as illustrated in Figure 19.

[0183] *Example 5: Formulation of coating fluid containing TIPSOCLMB 80 mg*
TIPSOCLMB 80 mg Irgacure 819 (Ciba Geigy; sensitizer) 4.0 ml CD-501 acrylate
(Sartomer; propoxylated[6] trimethylolpropanetriacrylate) 18.5 mg 1,4-diazabicyclo
[2.2.2]octane ("Dabco" Aldrich; base) 155 μ l 1,1,1,3,3,3-hexamethyldisilazane
("HMDZ" Aldrich) stabilizer) The TIPSOCLMB, Irgacure 819, and Dabco are weighed into
a brown glass bottle, a stir bar is added, the CD-501 is poured in to the proper
weight, and the HMDZ is added by syringe. Dry nitrogen is blown into the bottle for a
few minutes and the bottle is capped and the cap covered by parafilm. The contents
are stirred at room temperature for at least two hours to dissolve the solids. If not all
of the material is used, blow the bottle with nitrogen, cap and seal with parafilm, and
store in a freezer; warm the bottle before opening to prevent water from condensing
in the bottle.

[0184] *Example 6: Preparation of disk surface-coated with TIPSOCLMB/acrylate*
formulation A DVD clear half disk (an unmetalized 0.6 mm thick and 120 mm
diameter polycarbonate disc) or a full DVD (two layers bonded together, back to back
with an adhesive) is centered on a laboratory spin coating turntable rotating at roughly
60 rpm"s. A 4 ml solution from example #5 is then applied uniformly in a circular ring
by a syringe at about a 34 to 40 mm diameter from the center of the disc. The spin
speed is then rapidly increased to about 200 rpm for about 15 seconds, resulting in a
coating of acrylate/TIPSOCLMB fluid about five μ m thick. The spinning is slowed;
excess fluid wiped off of the edge of the disk with a tissue and base solvent, if
available, and then removed to a lab bench. At this point, the disc is subjected to
about five flashes from a Norlite 400 xenon flash lamp at its max setting. The time
between flashes is dictated by the charging of the flash lamp, but should be sufficient
as to not induce added stress from heat generated in the cure (typically about 5

seconds). This process will yield a clear, uncolored, fully cured acrylate film. Other disks are also prepared with similar acrylate formulations that contain either no Dabco or 10X the amount of Dabco described in Example 5.

[0185] *Example 7: Preparation of disk sandwich-coated with TIPSOCLMB/acrylate formulation* A DVD half disk is centered data side up on the turntable as stated above. The turntable is held stationary while the fluid is dispensed on the data side in a manner creating drops with a syringe roughly 3~5 mm round. These are evenly spaced about 3mm apart on a diameter of 30 ~40 mm. The disc to be bonded is then placed data side facing the solution and slightly bowed away from the bottom disc by the edges. The disc will be lowered at an angle until the first contact point between a fluid drop and top disc occurs. We do not want to place the top disc immediately on the bottom because of entrapped air and subsequent bubbles. Therefore, to get a more uniform capillary flow, we can rotate the disc in a clockwise rotation while keeping it slightly bent under light pressure until each of the fluid drops begins to form a capillary bridge ring. Once the capillary ring is completed, the top disc can be released and the capillary action will continue. We can wait for the capillary flow to cover the surface, or we can spin the disc at 100 rpm"s until the material at least reaches the maximum OD diameter. At this point the turntable can be turned on and rotated at about 500 rpm"s for 5 seconds. This will level the spacer layer (adhesive layer) and remove excess material from the OD. The disc edge can then be wiped and the disc will then be UV cured. It is important that prior to curing, the disc halves be aligned as close as possible to avoid center hole misalignment an subsequent play back problems. At this point, the disc is subjected to about 20~30 flashes from a Norlite 400 xenon flash lamp at its max setting. The time between flashes is dictated by the charging of the flash lamp, but should be sufficient as to not induce added stress from heat generated in the cure (Typically 5 seconds). This process will yield a clear, uncolored, fully cured acrylate film. Other disks are prepared with similar acrylate formulations that contain either no Dabco or 10X the amount of Dabco described in Example 5.

[0186] *Example 8: Deblocking and oxidation of TIPSOCLMB in surface and sandwich-coated disks, and the effect of a base included in the coating formulation* Disks prepared as described in Examples 6 and 7 were cut into six "chips" each and the

chips were stored in either dry nitrogen, dry air, or room air (average RH about 30%) and their cyan reflectance densities were recorded periodically with an X-Rite 504 densitometer (the samples stored in nitrogen were only tested at the start and end of the experiment as they were visibly unchanged and it was desired to minimize their exposure to oxygen). In all cases the samples stored in nitrogen showed no methylene blue (MB) generation, as expected. Incorporating 1,4-diazabicyclo[2.2.2]octane (Dabco) into an acrylate formulation at 1.0 equivalent with respect to the TIPSOCLMB gave very significant acceleration of the deblocking/oxidation rate compared to a control (Figure 18), while a higher concentration of this compound was actually less effective. In general the open samples (those with the TIPSOCLMB layer coated on top of a DVD half without any cover) generated MB only slightly faster than the sandwich structures, indicating that deblocking and oxidation of the LMB is not significantly limited by the transfer of either water or oxygen through an unmetallized 0.6 mm polycarbonate layer. Rather, the deblocking of the TIPSOCLMB is likely to be rate-limiting in these systems. The control samples without any added base shows noticeably faster MB generation in room air than in dry air, suggesting that moisture in the air speeds deblocking in this sample.

[0187] Example 9 illustrates how a reactive bonding layer was incorporated into Special DVD-5 Design #2, thus manufacturing a disc that was normally playable like a DVD-5 and subsequently became unplayable.

[0188] *Example 9: Incorporating TIPSOCLMB into a Special DVD-5 design #2 bonding layer* A set of experiments was performed to test whether a formulation containing TIPSOCLMB, Irgacure 819, Dabco, 1,1,1,3,3,3-hexamethyldisilazane (as a fluid stabilizer), and Sartomer CD-501 acrylate monomer could be used as a DVD adhesive to produce playable DVDs. Using the formulation described in Example 5, filtered through a 1.0 μ m glass syringe filter, the fluid was syringed onto either clear or metallized Special DVD-5 Design #2 halves manufactured as in Example 2. A DVD half disk is centered data side up on the turntable as stated above. The turntable is held stationary while the fluid is dispensed on the data side in a manner by creating drops with a syringe roughly 3~5 mm round. These are evenly spaced circularly about a diameter of 30 ~40 mm. The disc to be bonded is then placed data side facing the solution and slightly bowed away from the bottom disc by the edges. The disc will be

lowered at an angle until the first contact point between the fluid and top disc occurs. We do not want to place the top disc immediately on the bottom because of entrapped air and subsequent bubbles. Therefore, to get a more uniform capillary flow, we can rotate the disc in a clockwise rotation while keeping it slightly bent under light pressure until each of the fluid drops begins to form a capillary bridge ring. Once the capillary ring is completed, the top disc can be released and the capillary action will continue. We can wait for the capillary flow to cover the surface, or we can spin the disc at 100 rpm until the material reaches the maximum OD diameter. At this point the turntable can be turned up and rotated at about 500 rpm's for 5 seconds to thin out the adhesive and achieve a resulting 50 μ m adhesive films (determined by profilometry). This will level the spacer layer (adhesive layer) and remove excess material from the OD. The disc edge can then be wiped and then the disc UV cured. It is important that prior to curing, the disc halves be aligned as close as possible to avoid center hole misalignment and subsequent play back problems. At this point, the disc is subjected to about 20~30 flashes from a Norlite 400 xenon flash lamp at its max setting. The time between flashes is dictated by the charging of the flash lamp, but should be sufficient as to not induce added stress from heat generated in the cure (Typically 5 seconds). This process will yield a clear, uncolored, fully cured acrylate film that plays on the DVD test player.

[0189] The discs were manufactured under normal ambient conditions, and were subsequently put in a nitrogen box for 3-4 days, to remove the oxygen dissolved in the substrates (which would take an estimated 12-20 hours), and to allow TIPSOCLMB to unblock into LMB (which would take 2-3 days).

[0190] The Special DVD-5 design #2 discs were subsequently removed from the nitrogen box and were measured for reflectivity at the 650nm wavelength as a function of time. The discs were clear and playable for 12-16 hours after which time they turned dark blue within 24 hours and became unplayable with reflectivities under 2% at 650 nm.

[0191] *Multiple-layer optical discs* As seen in the DVD family illustration in Figure 4, in a dual layer optical disc designed to read multiple layers from one side, the spacer (bonding) layer is in the optical path. In the case of Dual Layer DVDs, the given specification for this spacer layer thickness is 0.055 +/- 0.015 mm. The thickness of

the substrate for a dual layer DVD with optical path bonding is typically 0.55 mm ~ 0.64 mm.

[0192] Incorporating a reactive compound inhibiting the reading laser in the bonding layer 800 of either type of dual-layer disc would only inhibit the player from reading the L1 layer 805, as the bonding layer 800 is not in the optical path for reading the L0 layer 810. Furthermore, the metal 815 in the L0 layer 810 might act as a barrier preventing a predetermined stimulus such as moisture or oxygen to permeate to the reactive compound in the bonding layer 800 in a controllable manner.

[0193] One method around this potential problem would be as follows. Typically, when a player or a drive begins reading a disc, it looks for the table of contents or information area in the lead-in area for the L0 layer 810 (see Figure 6). When authoring the disc, it is possible to have the L0 lead-in 820 area contain commands to directly access the L1 layer 805. In order to be able to read the L0 layer 810 to direct the play sequence to the L1 805, we would have to metallize the L0 side 810. This would then possibly interfere with the reactive adhesive material 800 causing unstable or uncontrolled kinetics of reaction that would be dependent on the permeability of the metal layer. One approach around this would be to change the metallizer masking for the L0 semi-reflective layer 800, which is typically run out to 58 mm to 59 mm radius on the disc, to something closer to the lead-in or information data area on the L0.

[0194] To facilitate activation of the reactive material 800, e.g., when the activating stimulus is oxygen or moisture that might be prevented from reaching the reactive bonding layer 800 because of the L0 metal layer 820, part of the L0 layer 810 can be masked during metallization, so that part of the reactive layer will be easier to expose to the stimulus and thus the corresponding part of the L0 layer will be disabled. These discs would have a partially metallized L0 layer 810, as illustrated in Figure 20. For example, if only the lead-in area or program start portion of the L0 layer 810 is metallized, the player is able to read the lead-in data, and is able to access the information stored on L1 layer 805. As only a small area on the L0 layer 810 would be metallized, a substantial part of the reactive bonding layer would be in direct contact with the L0 substrate 810, which is typically permeable by stimuli such as oxygen or

moisture. When the reactive bonding layer responds to the appropriate stimuli and starts interfering with the reading laser, the player is no longer able to access the corresponding part of the L1 layer 805.

[0195] Another embodiment of the present invention is utilizing authoring techniques, such as sequencing and branching commands to be executed by the optical media player, to ensure that making a certain part of a disc unplayable will interfere with playing other parts of the disc, or the entire disc. The part of the disc made unplayable for this purpose may be in the single layer of a one-layer disc, or in any of the layers of a multi-layer disc. For example, one embodiment of this invention consists of a DVD-9 authored so that making a certain part of the L1 layer unplayable would interfere with playing other parts of the disc, or the entirety of the disc. For example, reading the L0 layer lead-in area would direct the player to access a part of the L1 layer that would become unreadable when the reactive layer starts interfering with the reading laser, which would cause the disc to be inoperable. A DVD-9 disc can be authored so that all or part of the L1 layer is essential in order to play any information on L0 and/or L1. For example each chapter on the disc can be authored so that it requires reading certain information on L1 before proceeding.

[0196] In another embodiment of this invention, activation of the reactive material is facilitated by controlling the deposition of the L0 layer. For example, fast deposition of a gold or silver or silicon L0 layer through sputtering is known to result in grainy dendritic formations that are easier to penetrate by oxygen and moisture. Also, a thinner L0 layer can be deposited, which is easier to penetrate by oxygen and moisture. While depositing grainy or thin L0 layers may be unacceptable for a permanent, archival quality disc, it is often adequate for a limited use, expiring disc.

[0197] *Example 10: DVD-9 discs with TIPSOCLMB incorporated in a reactive bonding layer*
A DVD-9 with parallel track path encoding can have two distinctly different layers for play back. In the encoding or data mastering process, the Lead-in area normally found on the L0 disc, can have information telling the reading players to read from either or both layers on the disc. Therefore, for this example using a reactive bonding material, the reactive layer could prevent play back from the L1 layer while not affecting the L0. For this example corresponding L0 and L1 masters were manufactured, and L0 and L1

substrates were normally molded and metallized.

[0198] The DVD halves were bonded as in example 9 above using an adhesive containing the formulation TIPSOCLMB, Irgacure 819, Dabco, 1,1,1,3,3,3-hexamethyldisilazane (as a fluid stabilizer), and Sartomer CD-501 acrylate monomer described in Example 5. The solution was filtered through a 1.0- μ m glass syringe filter. A DVD half disk is centered data side up on the turntable as stated above. The turntable is held stationary while the fluid is dispensed on the data side in a manner by creating drops with a syringe roughly 3~5 mm round. These are evenly spaced circularly about a diameter of 30 ~40 mm. The disc to be bonded is then placed data side facing the solution and slightly bowed away from the bottom disc by the edges. The disc will be lowered at an angle until the first contact point between the fluid and top disc occurs. We do not want to place the top disc immediately on the bottom because of entrapped air and subsequent bubbles. Therefore, to get a more uniform capillary flow, we can rotate the disc in a clockwise rotation while keeping it slightly bent under light pressure until each of the fluid drops begins to form a capillary bridge ring. Once the capillary ring is completed, the top disc can be released and the capillary action will continue. We can wait for the capillary flow to cover the surface, or we can spin the disc at 100 rpm until the material reaches the maximum OD diameter. At this point the turntable can be turned up and rotated at about 500 rpm"s for 5 seconds to thin out the adhesive and achieve a resulting 50 μ m adhesive films (determined by profilometry). This will level the spacer layer (adhesive layer) and remove excess material from the OD. The disc edge can then be wiped and then the disc UV cured. It is important that prior to curing, the disc halves be aligned as close as possible to avoid center hole misalignment an subsequent play back problems. At this point, the disc is subjected to about 20~30 flashes from a Norlite 400 xenon flash lamp at its max setting. The time between flashes is dictated by the charging of the flash lamp, but should be sufficient as to not induce added stress from heat generated in the cure (Typically 5 seconds). This process will yield a clear, uncolored, fully cured acrylate film that plays on the DVD test player.

[0199] The discs were manufactured under normal ambient conditions, and were subsequently put in a nitrogen box for 7 days, to remove the oxygen dissolved in the substrates (which would take an estimated 12~20 hours), and to allow TIPSOCLMB to

unblock into LMB (which was estimated to take up to 5-6 days). The discs were subsequently removed from the nitrogen box and were normally playable on both the L0 and L1 layer for 2-3 days on a Pioneer player. After 7 days of exposure to ambient oxygen, the discs became unplayable on the L1 layer, although they would play normally on the L0 layer.

[0200] *Example 11: DVD-9 discs with partially metallized L0 layer* As in example 10 above, DVD-9 master tapes were generated with the data area being identified on layer L1 and the L0 layer serving only to provide the lead-in and subsequent table of contents relating to the disc type and information. During play back, the L0 lead-in would instruct the disc to read from the L1 data side. In this case, we would not have to metalize the entire surface of the L0 layer because there is no information to be read outside of the lead-in area. Therefore, DVD-9 master tapes were produced with lead-in and command information on L0 and data area on L1. Typically, the metalizer masking covers areas from 25 mm through 118 mm diameters on both layers. Being as the lead-in area data covers the diameters of 25.2 mm to a maximum of 48 mm, and the subsequent information area starts at no less than 48 mm diameter, the metalizer masking can be reduced to cover the lead-in only. This would allow a reflective signal to read the lead-in on the L0 layer and then switch to the L1 layer for data playback without having to read through additional semi-reflective metal.

[0201] In this example, we manufactured donut-masking plates that dropped into the metalizer OD mask assembly. By registering the masking from the OD, we are able to reduce the metalized diameter to an area allowing lead-in playback. We extended the mask just outside of the lead-in 48 mm diameter in order to compensate for eccentricity tolerance with the masking position. Additionally, in order to prevent a reflective spike from the transition of clear disc area to metalized disc area when reading the L1 layer, the edge of the masking was slightly raised above the disc to cause a shadowing or tapered layer uniformity. This would cause a gradual focusing compensation rather than a large "speed bump" effect causing its radial noise and focusing error to fall out of specification and perhaps jump track.

[0202] The resulting DVD-9 halves were bonded as in Example 10. The DVD-9s constructed were tested for playability in a Pioneer DVD player and in a DVD-ROM

drive, and were subsequently put in a nitrogen box for 7 days, so that the TIPSOCLMB would unblock into LMB. The discs were subsequently removed from the nitrogen box and were clear and playable for 12–16 hours, and turned dark blue within 24 hours after that, becoming unplayable. The discs were effectively prevented from having information read from either L0 or L1.

[0203] *Controlling the timing of the reaction* Preferably, the data quality of the disc should remain high for the intended period of use and then decay rapidly resulting in a rapid degradation of the ability to read data off the optical disc. One benefit of this embodiment of the present invention is that for a broad class of stimuli, such as those requiring diffusion of a substance through a barrier layer, incorporating the reactive material in an interstitial layer results in substantial advantages regarding the timing characteristics of the reaction.

[0204] One method of achieving the above mentioned desirable timing characteristics is to use a reactive interstitial material between the disc substrates, as described earlier, which reacts with a substance that needs to diffuse through the substrates of the disc. For example, if the reactive material is sensitive to oxygen, there will be an extended period in which there will be no reaction while the oxygen diffuses through the disc substrates. Once oxygen reaches the reactive layer, the resulting reaction can be fast, resulting in rapid expiration of the disc.

[0205] When oxygen is used as the diffusing substance, it may be necessary to remove oxygen that dissolves in the disc during the different stages of its manufacture. This can be done, for example, by storing the discs in a vacuum or in an oxygen free environment for an appropriate period of time. It has been established theoretically and experimentally that 24 hours is an adequate period to extricate oxygen dissolved in a 0.6 mm thick polycarbonate disc substrate. Alternatively, if a blocked reactive material is used as described earlier, an oxygen scavenging material, such as iron or an organometallic compound, can be used to extricate oxygen from the optical disc before the blocked reactive material unblocks. This method has several manufacturing advantages; for example, it can avoid oxygen extrication during manufacturing of the disc by including the oxygen scavenging material in the packaging of the disc, which allows the extrication of the oxygen to take place after the disc is manufactured and

packaged.

[0206] Another means for controlling the timing of the expiration of the disc is to include in or adjacent to the reactive layer a finite, controlled quantity of an appropriate protective substance, such as an antioxidant in the case that the reactive layer reacts with oxygen. The protective substance would prevent the reactions that cause the disc to expire until such time as the anti-oxidant was consumed, at which time the disc would rapidly degrade and become unplayable. For example, an organometallic compound that reacts with oxygen can be packaged with the disc to protect the disc from oxidation while in the package. Alternatively, the organometallic compound can be incorporated into the substrate, thus continuing to protect the metal layer for a period of time after the package has been opened.

[0207] Depletion of a protective substance could be combined with diffusion of the triggering substance through the substrate of the disc, to result in longer delays before the disc expires, or to enable finer control of the characteristics of the expiration process, such as the steepness of reflectivity degradation.

[0208] Example of antioxidant in reactive layerThe addition of a 4% concentration of stannous ethylhexanoate into a typical TLMB containing active adhesive DVD provides a disc with play time of about 24 hours, whereas discs made using the same formulation without added reducing agent provide a play time of about 8 hours. Indeed, the play time can be adjusted over a wide range by varying the amount of reducing agent (see Table I).

[t4]

Formulation #	Concentration		Play Time (hrs)	
	TLMB	Sn(II)	short	long
A	1%	2%	14	22
B	1%	4%	38	55
C	0.5%	2%	18	26
D	0.5%	4%	46	58

Table I

[0209] DVD-5 discs were made using a TLMB formulation similar to the above Examples, and deblocked in an oxygen-free atmosphere for 48 hours at 60 ° C. At that time the discs were exposed to ambient room air and the methylene blue color development was quantified with an X-Rite reflection densitometer. The short play time was chosen

to be the time at which the cyan density increased by 0.35, which roughly corresponds to a playability cutoff at 45% reflectance as typified by a low quality DVD player. The long play time was chosen to be the time at which the cyan density increased by 0.85, which roughly corresponds to a playability cutoff at 10% reflectance as typified by a high quality DVD player.

[0210] The most likely mechanism for this extended play is reduction of the initially formed methylene blue dye back to the leuco form until most of the reducing agent is consumed. Alternate mechanisms, such as the stannous compound acting as a primary oxygen scavenger to consume oxygen before the leuco dye is affected, are also possible.

[0211] The mobility within the cured matrix is expected to have a significant effect upon the reduction rate; indeed, the calculated glass transition temperature (T_g) of the monomers used in the above Examples is 34 ° C. In such a soft matrix, adequate molecular mobility should exist to allow contact of reducing agent and dye molecules.

[0212] Alternate reducing agents might include other Sn(II) compounds which would be soluble in the UV cure formulation, such as acetylacetonate chelates, fatty alpha-aminoacid chelates and salts; soluble iron(II) compounds, such as fatty carboxylates and chelates such as acetylacetonates; reducing saccharides; ascorbic acid and its derivatives such as ascorbyl palmitate; hydroxylamines; hydrazines; dithionates with a solubilizing counterion; alpha-hydroxyketones, such as acetol; appropriately substituted boron hydrides.

[0213] Optical media players are typically engineered with the ability to play previous generations of discs. For example, while CD players employ a laser with a wavelength of 780 nanometers to read CDs, DVD players typically employ their reading laser with a wavelength of 650 nanometers to read CD discs. The next generation DVDs ("blue laser DVDs") is designed to be read with a laser with a wavelength of 450-460 nanometers; the "DVR" format will use lasers emitting around 405 nm. Future generation players are likely to be able to read current DVDs with their 450-460 nanometer or 405 nanometer lasers.

[0214] Dyes used to inhibit the reading laser in current optical disc players are typically

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[0217] *Use of additional mechanism(s) to prevent recovery of data* Another embodiment of the present invention is combining the mechanism(s) that prevent reading of the optical disc by inhibiting the reading laser with additional mechanism(s) for preventing recovery of the information encoded in the data structures on the disc. These additional mechanism(s) can be designed with less accurate control of the timing of their activation than the mechanism(s) that work by inhibiting the reading laser. Thus it may be desirable to combine the mechanism that controls expiration of the optical disc by interfering with the reading laser with additional mechanism(s) that permanently prevent the recovery of the data on the optical disc. For example, a disc may become unplayable by transitioning a layer in the optical path from transparent to opaque in a controlled time period, for example approximately 24 hours after a predetermined stimulus, such as removing the disc from its packaging. In addition, a secondary mechanism could corrode the metal layer on the disc, such mechanism acting over a longer period of time, such as 1–2 weeks, and being triggered by the same or a different stimulus. Additional mechanisms may also be employed, such as an additive that degrades the polycarbonate material from which the disc is composed, which process can be triggered by the same stimulus (such as exposure to ambient air), or a different stimulus (such as the centrifugal forces generated when a disc is played in a CD or DVD player). Other triggering stimuli for these backup mechanisms can include various constituents of air, light, physical motion, and time from manufacturing or packaging. Many other mechanisms are possible.

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from the information bearing aluminum layer by a material incorporated for this purpose, or by an existing material, such as the bonding layer or one of the substrates of the optical disc. This silver layer can be above or below the aluminum layer, and if is below (and thus in the optical path of the reading laser) it needs to be sufficiently transparent initially so that the reading laser can read the information on the aluminum layer.

[0219] In one embodiment of the invention, a DVD-9 disc is manufactured with a reactive bonding layer consisting of a material with appropriate dielectric properties, and with appropriate selection of metals for L0 and L1. For example, L0 can be made of silver and L1 can be made of aluminum.

[0220] When a silver layer and an aluminum layer are separated by an appropriate dielectric material, then upon exposure to oxygen the silver serves as a cathode, on which O_2 is reduced, and aluminum serves as an anode. Corrosion is fast only if a short develops between the silver and the aluminum layers. The development of the short results from the growth of a silver dendrite through the separating material. To grow the dendrite through the separating material it is desirable to use a material that has some ionic conductivity. Several likely separating materials consist of or contain polyacrylate. If the polyacrylate is slightly hydrolyzed, or if it is, for example, a 2-hydroxyethylacrylate copolymer, there will be some ionic conductivity. Preferred are co-polymers of poly(acrylonitrile), or of poly(4-vinylpyridine), or of poly(l-vinylimidazole). All of these should conduct silver, copper or thallium ions (Ag^+ , Cu^+ or Tl^+). Thallium is less preferred due to its toxicity.

[0221] The chemical equations are as follows: Silver is air-oxidized: $4Ag + O_2 \rightarrow Ag_2O$
(complexed with lacquer) $Ag_2O + H_2O + \text{complexant} \rightarrow 2Ag^+ \text{ (complexed)} + 2OH^-$
 Ag^+ is reduced by aluminum, which is oxidized (if Ag^+ is mobile in the lacquer, which is designed to conduct Ag^+) $Ag^+ + Al \rightarrow Al^{3+} + 3Ag$
 $Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \rightarrow Al(O)OH + H_2O$ A silver dendrite starts growing from the aluminum to the silver. When the two layers are shorted, the "switch" between a battery's (Al) anode and (Ag) cathode is closed. Corrosion is rapid and catastrophic. One skilled in the art will recognize that other similar metals may be substituted for Al and Ag in this example.

- [0222] Alternatively, other ways of permanently corroding data layers via the reactive layer can be employed. For example, certain embodiments of this invention may have a bonding layer that promotes the corrosion of the reflective metal layer or may involve the diffusion of some substance from the bonding layer to the reflective layer (s). In other embodiments, the additional mechanisms will not be part of the bonding material. For example, a precursor of a corrosive substance may be deposited adjacent to the metal layer. When oxygen or some other appropriate substance diffuses through the substrate and reaches the corrosive precursor, a reaction could be initiated that results in producing a corrosive substance that over a period of time permanently destroys the data structures on the disc. Alternatively, the material in the substrate of the disc, such as polycarbonate, could be engineered so that it degrades over a period of time, thus making the disc unusable. Such substances and reactions are known to the skilled in the art.
- [0223] Another composition that performs a similar function is one in which the substrate itself is modified over time. The modification of the substrate could cause it to change its optical qualities, thereby degrading the signal reaching the reader. These optical qualities could include its index of refraction or its transparency.
- [0224] Moreover, the modification of the substrate could cause the underlying metal layer to change its optical properties, as described above. In this way, a time-sensitive substrate and/or lacquer could be combined with a reflective layer that becomes non-reflective.
- [0225] The transparency of a polymer film can be changed by any of the following: reaction of the film with water; reaction of the film with oxygen; or crystallization of the polymer, meaning increased alignment of polymer molecules in the film.
- [0226] As an example, a substrate could be chosen that is changed by components in air such as oxygen or water. For example, oxygen could oxidize the substrate, causing a change in its transparency or its index of refraction. Alternatively, the substrate could be designed to absorb water in the air, causing it to swell and change its optical properties. Another example is that the substrate could change its permeability to oxygen over time, thereby permitting the oxidation of the metallic layer. In the later case, the overall time sensitivity of the optical media could be a function of the

properties of both the substrate and/or lacquer and the reflective layer.

[0227] The substrate or the metallic layer could also be made sensitive to specific wavelengths of light. Exposure to these wavelengths would cause a change in the optical qualities of the layer, thereby degrading the signal reaching the reader. Examples include photodepolymerization of the substrate; photogeneration of acid; photogeneration of singlet oxygen; and unzipping of the polymers (e.g., fissure of cross linking hydrogen bonds). Incorporation of light-activated catalysts into the substrate or the metallic layer can assist in this process.

[0228] Accordingly, the present invention has been described at some degree of particularity directed to the exemplary embodiments of the present invention. It should be appreciated, though, that the present invention is defined by the following claims construed in light of the prior art so that modifications or changes may be made to the exemplary embodiments of the present invention without departing from the inventive concepts contained herein.